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GENERAL CHEMISTRY: ATOMS FIRST

Chapter 12 Chemical Kinetics

Prentice Hall

Kinetics

- kinetics is the study of the factors that affect the speed of a reaction and the mechanism by which a reaction proceeds.
- experimentally it is shown that there are 4 factors that influence the speed of a reaction:
  - **nature of the reactants,**
  - **temperature,**
  - **catalysts,**
  - **concentration**

The reaction between sodium and bromine

or

The rusting of iron?

Reaction Rates

Chemical Kinetics: The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur.
> **rate** is how much a quantity changes in a given period of time

- for reactants, a negative sign is placed in front of the definition, because their concentration is decreasing:
- for products, a positive sign is used, because their concentration is increasing:

$$\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

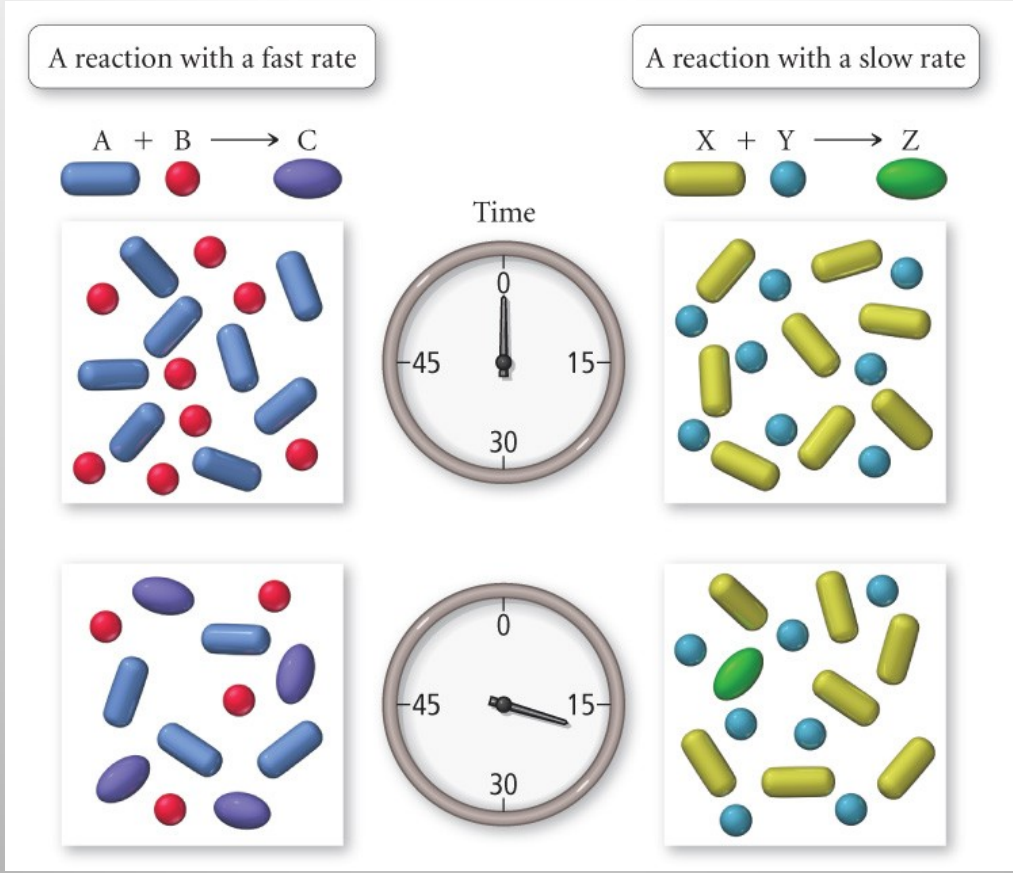
$$\text{Rate} = \frac{\Delta[\text{product}]}{\Delta \text{time}} = -\frac{\Delta[\text{reactant}]}{\Delta \text{time}}$$

Reaction Rate Changes Over Time

- as time goes on, the rate of a reaction generally slows down
  - because the concentration of the reactants decreases.
- at some time the reaction stops, either because the reactants run out or because the system has reached equilibrium.

at t = 0
[A] = 8
[B] = 8
[C] = 0

at t = 16
[A] = 4
[B] = 4
[C] = 4



at t = 0
[X] = 8
[Y] = 8
[Z] = 0

at t = 16
[X] = 7
[Y] = 7
[Z] = 1

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$

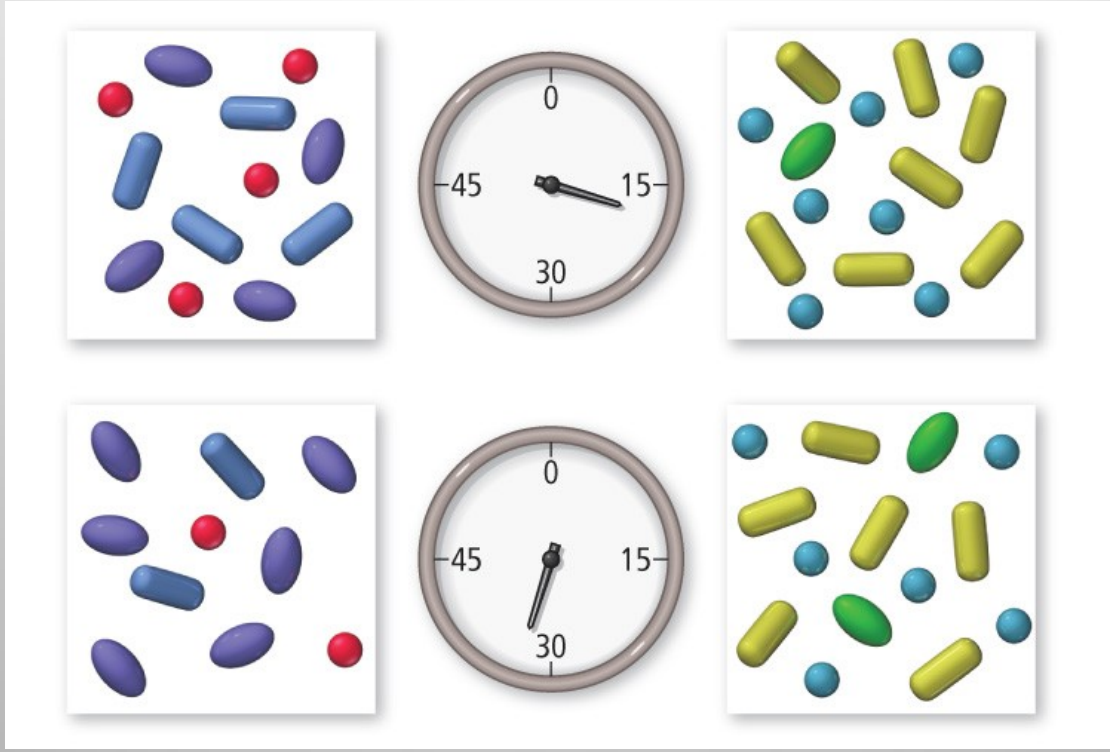
$$\text{Rate} = -\frac{(4 - 8)}{(16 - 0)} = 0.25$$

$$\text{Rate} = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$

$$\text{Rate} = \frac{(1 - 0)}{(16 - 0)} = 0.0625$$

at t = 16
[A] = 4
[B] = 4
[C] = 4

at t = 32
[A] = 2
[B] = 2
[C] = 6



at t = 16
[X] = 7
[Y] = 7
[Z] = 1

at t = 32
[X] = 6
[Y] = 6
[Z] = 2

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$

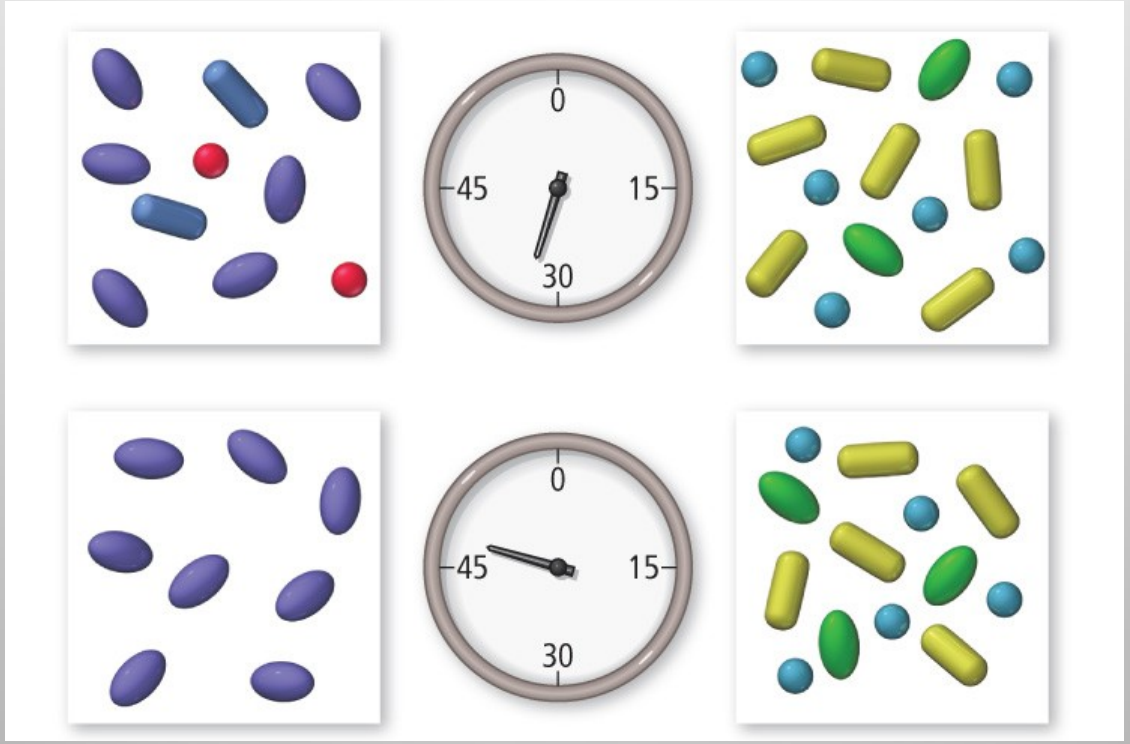
$$\text{Rate} = -\frac{(2-4)}{(32-16)} = 0.125$$

$$\text{Rate} = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$

$$\text{Rate} = \frac{(2-1)}{(32-16)} = 0.0625$$

at t = 32
[A] = 2
[B] = 2
[C] = 6

at t = 48
[A] = 0
[B] = 0
[C] = 8



at t = 32
[X] = 6
[Y] = 6
[Z] = 2

at t = 48
[X] = 5
[Y] = 5
[Z] = 3

$$Rate = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$

$$Rate = -\frac{(0-2)}{(48-32)} = 0.125$$

$$Rate = -\frac{(5-6)}{(48-32)} = 0.0625$$

$$Rate = \frac{\Delta[C]}{\Delta t} = \frac{([C]_2 - [C]_1)}{(t_2 - t_1)}$$

$$Rate = \frac{(3-2)}{(48-32)} = 0.0625$$

$$Rate = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$

$$Rate = \frac{(8-6)}{(48-32)} = 0.125$$

Rate Law

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant.

General rate of reaction:

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow d\,\mathrm{D} + e\,\mathrm{E}$$

$$\text{rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t} = \frac{1}{e}\frac{\Delta[\mathrm{E}]}{\Delta t}$$

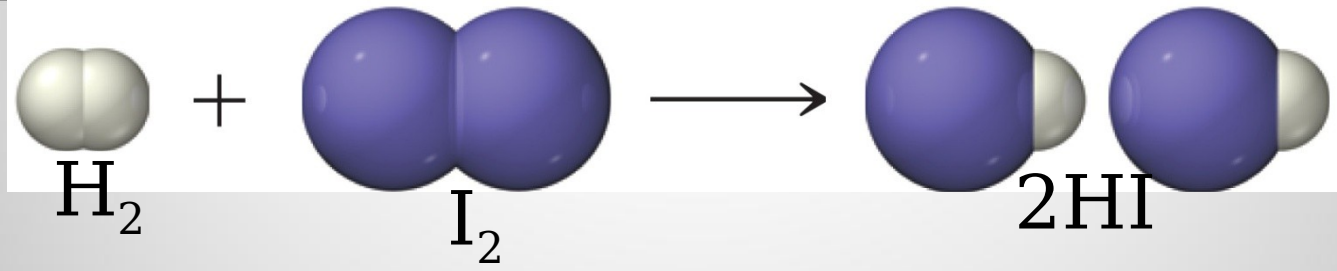
Reaction Rate and Stoichiometry

- in most reactions, the coefficients of the balanced equation are not all the same

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$$

- for these reactions, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another
  - ✓ for the above reaction, for every 1 mole of H_2 used, 1 mole of I_2 will also be used and 2 moles of HI made
  - ✓ therefore the rate of change will be different
- in order to be consistent, the change in the concentration of each substance is multiplied by 1/coefficient

$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = +\left(\frac{1}{2}\right)\frac{\Delta[HI]}{\Delta t}$$

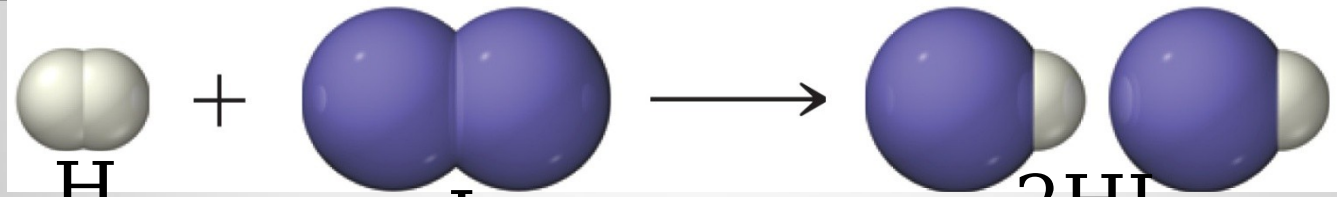


Time (s)	$[H_2]$, M	[HI], M	Avg. Rate, M/s $-\Delta[H_2]/\Delta t$	Avg. Rate, M/s $1/2\ \Delta[HI]/\Delta t$
0.000	1.000			
10.000	0.819			
20.000	0.670			
30.000	0.549			
40.000	0.449			
50.000	0.368			
60.000	0.301			
70.000	0.247			
80.000	0.202			
90.000	0.165			
100.000	0.135			

Stoichiometry tells us that for every 1 mole/L of H_2 used, 2 moles/L of HI are made.

Assuming a 1 L container, at 10 s, we used 1.000 – 0.819 = 0.181 moles of H_2. Therefore the amount of HI made is 2(0.181 moles) = 0.362 moles

At 60 s, we used 1.000 – 0.301 = 0.699 moles of H_2. Therefore the amount of HI made is 2(0.699 moles) = 1.398 moles

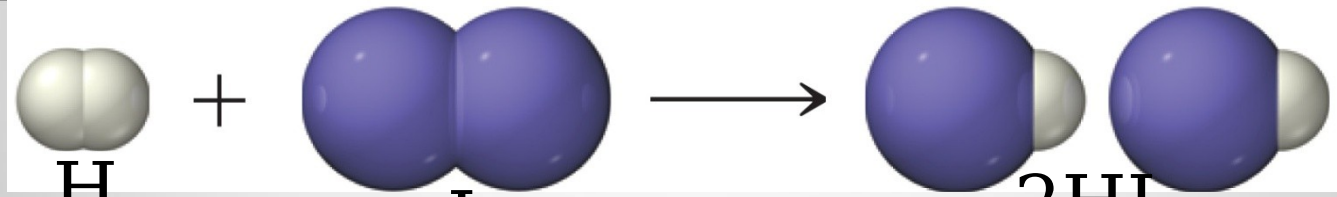


Time (s)	$[H_2]$, M	[HI], M	Avg. Rate, M/s $-\Delta[H_2]/\Delta t$	Avg. Rate, M/s $1/2\ \Delta[HI]/\Delta t$
0.000	1.000	0.000		
10.000	0.819	0.362		
20.000	0.670	0.660		
30.000	0.549	0.902		
40.000	0.449	1.102		
50.000	0.368	1.264		
60.000	0.301	1.398		
70.000	0.247	1.506		
80.000	0.202	1.596		
90.000	0.165	1.670		
100.000	0.135	1.730		

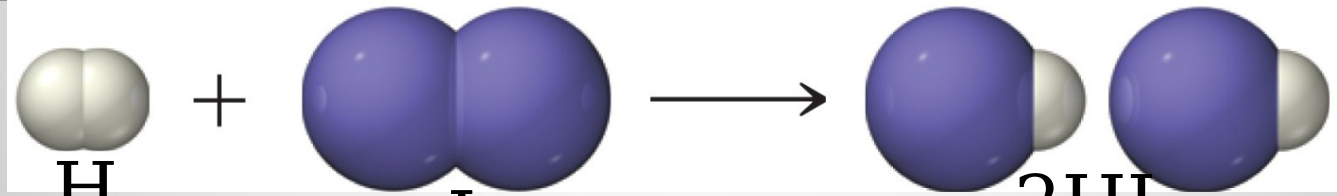
The average rate is the change in the concentration in a given time period.

In the first 10 s, the $\Delta[H_2]$ is -0.181 M, so the rate is

$$-\frac{-0.181\ \text{M}}{10.000\ \text{s}} = 0.0181\ \frac{\text{M}}{\text{s}}$$



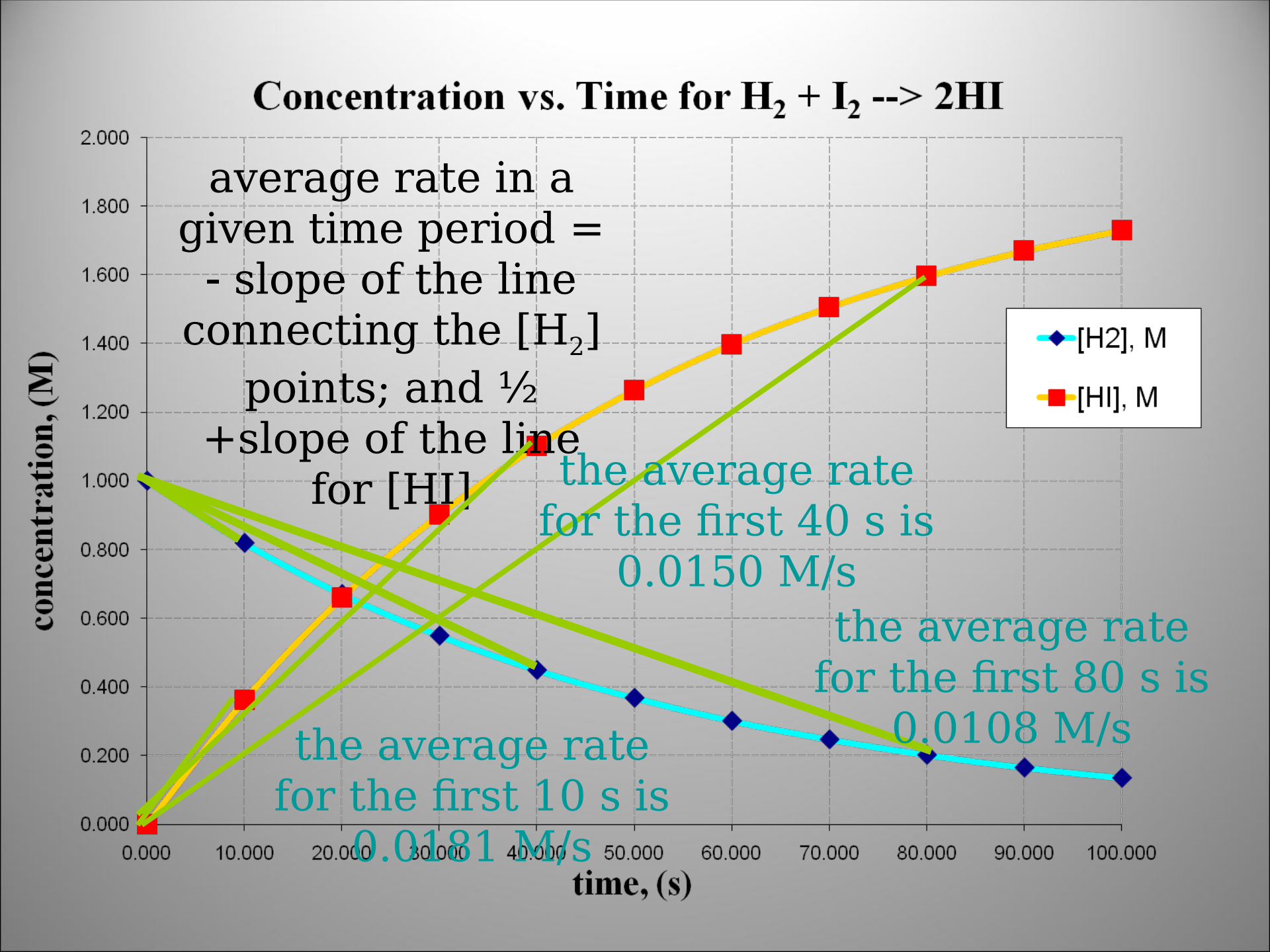
Time (s)	$[H_2]$, M	[HI], M	Avg. Rate, M/s $-\Delta[H_2]/\Delta t$
0.000	1.000	0.000	
10.000	0.819	0.362	0.0181
20.000	0.670	0.660	0.0149
30.000	0.549	0.902	0.0121
40.000	0.449	1.102	0.0100
50.000	0.368	1.264	0.0081
60.000	0.301	1.398	0.0067
70.000	0.247	1.506	0.0054
80.000	0.202	1.596	0.0045
90.000	0.165	1.670	0.0037
100.000	0.135	1.730	0.0030



Time (s)	$[H_2]$, M	[HI], M	Avg. Rate, M/s $-\Delta[H_2]/\Delta t$	Avg. Rate, M/s $1/2\ \Delta[HI]/\Delta t$
0.000	1.000	0.000		
10.000	0.819	0.362	0.0181	0.0181
20.000	0.670	0.660	0.0149	0.0149
30.000	0.549	0.902	0.0121	0.0121
40.000	0.449	1.102	0.0100	0.0100
50.000	0.368	1.264	0.0081	0.0081
60.000	0.301	1.398	0.0067	0.0067
70.000	0.247	1.506	0.0054	0.0054
80.000	0.202	1.596	0.0045	0.0045
90.000	0.165	1.670	0.0037	0.0037
100.000	0.135	1.730	0.0030	0.0030

Average Rate

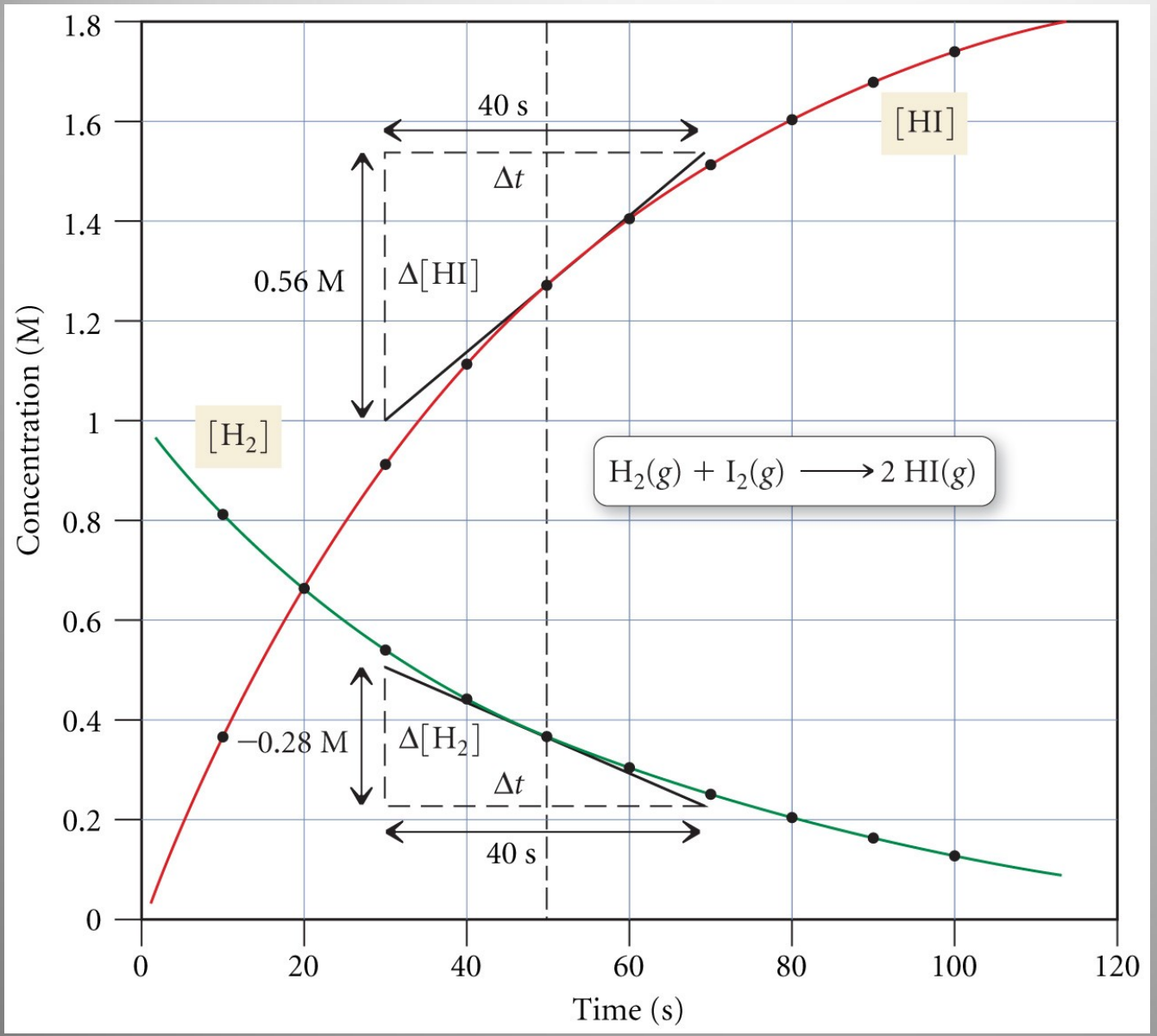
- the average rate is the change in measured concentrations in any particular time period
  - linear approximation of a curve
- the larger the time interval, the more the average rate deviates from the instantaneous rate


Concentration vs. Time for $H_2 + I_2$ --> 2HI
average rate in a given time period = - slope of the line connecting the [H_2] points; and ½ +slope of the line for [HI]
the average rate for the first 40 s is 0.0150 M/s
the average rate for the first 80 s is 0.0108 M/s
the average rate for the first 10 s is 0.0181 M/s
[H2], M
[HI], M
concentration, (M)
time, (s)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0.000
10.000
20.000
30.000
40.000
50.000
60.000
70.000
80.000
90.000
100.000

Instantaneous Rate

- the instantaneous rate is the change in concentration at any one particular time
  - slope at one point of a curve
- determined by taking the slope of a line tangent to the curve at that particular point
  - first derivative of the function

$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{\,(g)}$



Using $[H_2]$, the instantaneous rate at 50 s is:

$$Rate = -\frac{-0.28M}{40s}$$

$$Rate = 0.0070\frac{M}{s}$$

Using [HI], the instantaneous rate at 50 s is:

$$Rate = \left(\frac{1}{2}\right)\frac{0.56M}{40s}$$

$$Rate = 0.0070\frac{M}{s}$$

For the reaction given, the $[I^-]$ changes from 1.000 M to 0.868 M in the first 10 s. Calculate the average rate in the first 10 s and the $\Delta[H^+]$.

$$H_2O_{2\,(aq)} + 3\,I^-_{(aq)} + 2\,H^+_{(aq)} \rightarrow I^-_{3\,(aq)} + 2\,H_2O_{(l)}$$

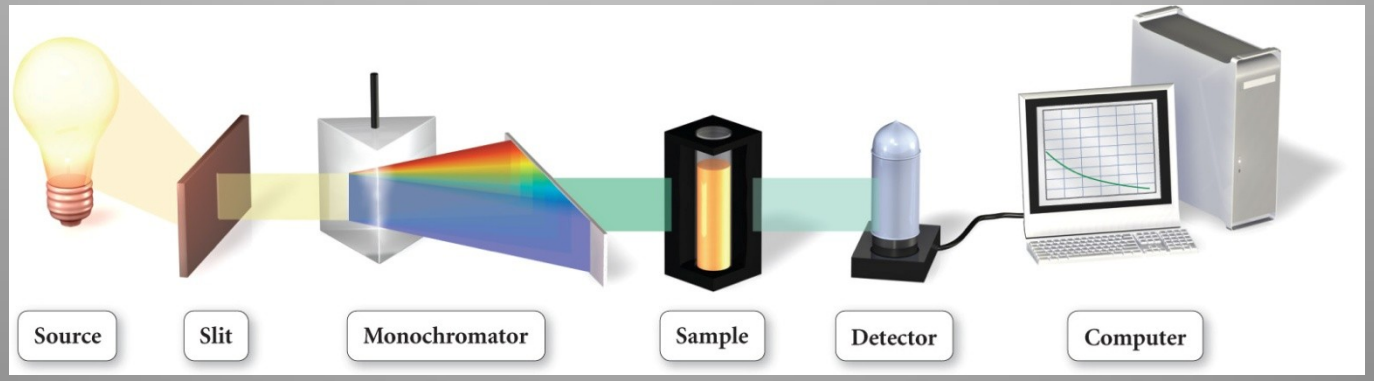
Solve the equation for the Rate (in terms of the change in concentration of the Given quantity)	$\text{Rate} = -\left(\frac{1}{3}\right)\frac{\Delta[I^-]}{\Delta t} = -\left(\frac{1}{3}\right)\frac{(0.868\,\text{M} - 1.000\,\text{M})}{10\,\text{s}}$ $\text{Rate} = 4.40\times10^{-3}\,\frac{\text{M}}{\text{s}}$ $\text{Rate} = -\left(\frac{1}{2}\right)\frac{\Delta[H^+]}{\Delta t}$
Solve the equation of the Rate (in terms of the change in the concentration	$\frac{\Delta[H^+]}{\Delta t} = -2(\text{Rate})$ $\frac{\Delta[H^+]}{\Delta t} = -2\left(4.40\times10^{-3}\,\frac{\text{M}}{\text{s}}\right) = -8.80\times10^{-3}\,\frac{\text{M}}{\text{s}}$

Measuring Reaction Rate

- in order to measure the reaction rate you need to be able to measure the concentration of at least one component in the mixture at many points in time
- there are two ways of approaching this problem (1) for reactions that are complete in less than 1 hour, it is best to use continuous monitoring of the concentration, or (2) for reactions that happen over a very long time, sampling of the mixture at various times can be used
  - when sampling is used, often the reaction in the sample is stopped by a quenching technique

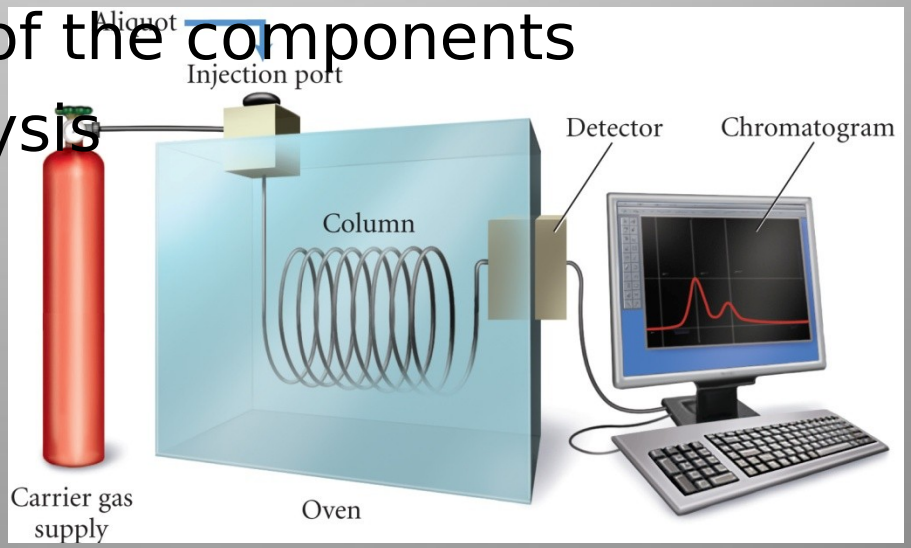
Continuous Monitoring

- **polarimetry** – measuring the change in the degree of rotation of plane-polarized light caused by one of the components over time
- **spectrophotometry** – measuring the amount of light of a particular wavelength absorbed by one component over time
  - the component absorbs its complimentary color
- **total pressure** – the total pressure of a gas mixture is stoichiometrically related to partial pressures of the gases in the reaction



Sampling

- **gas chromatography** can measure the concentrations of various components in a mixture
  - for samples that have volatile components
  - separates mixture by adherence to a surface
- drawing off periodic **aliquots** from the mixture and doing quantitative analysis
  - titration for one of the components
  - gravimetric analysis



Factors Affecting Reaction Rate - Nature of the Reactants

- nature of the reactants means what kind of reactant molecules and what physical condition they are in.
  - small molecules tend to react faster than large molecules;
  - gases tend to react faster than liquids which react faster than solids;
  - powdered solids are more reactive than “blocks”
    - more surface area for contact with other reactants
  - certain types of chemicals are more reactive than others
    - e.g., the activity series of metals
  - ions react faster than molecules
    - no bonds need to be broken

Factors Affecting Reaction Rate - Temperature

- increasing temperature increases reaction rate
  - chemist's rule of thumb - for each 10°C rise in temperature, the speed of the reaction doubles
    - for many reactions
- there is a mathematical relationship between the absolute temperature and the speed of a reaction discovered by Svante Arrhenius which will be examined later

Factors Affecting Reaction Rate - Catalysts

- catalysts are substances which affect the speed of a reaction **without being consumed.**
- most catalysts are used to speed up a reaction, these are called positive catalysts
  - catalysts used to slow a reaction are called negative catalysts.
- homogeneous = present in same phase
- heterogeneous = present in different phase
- how catalysts work will be examined later

Factors Affecting Reaction Rate

Reactant Concentration***

- generally, the larger the concentration of reactant molecules, the faster the reaction
  - Higher concentration increases the frequency of reactant molecule contact
  - concentration of gases depends on the partial pressure of the gas
    - higher pressure = higher concentration
- concentration of solutions depends on the molarity

Reaction Order

- the exponent on each reactant in the rate law is called the **order** with respect to that reactant
- the sum of the exponents on the reactants is called the **order of the reaction**
- The rate law for the reaction:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

is Rate = $k[NO]^2[O_2]$

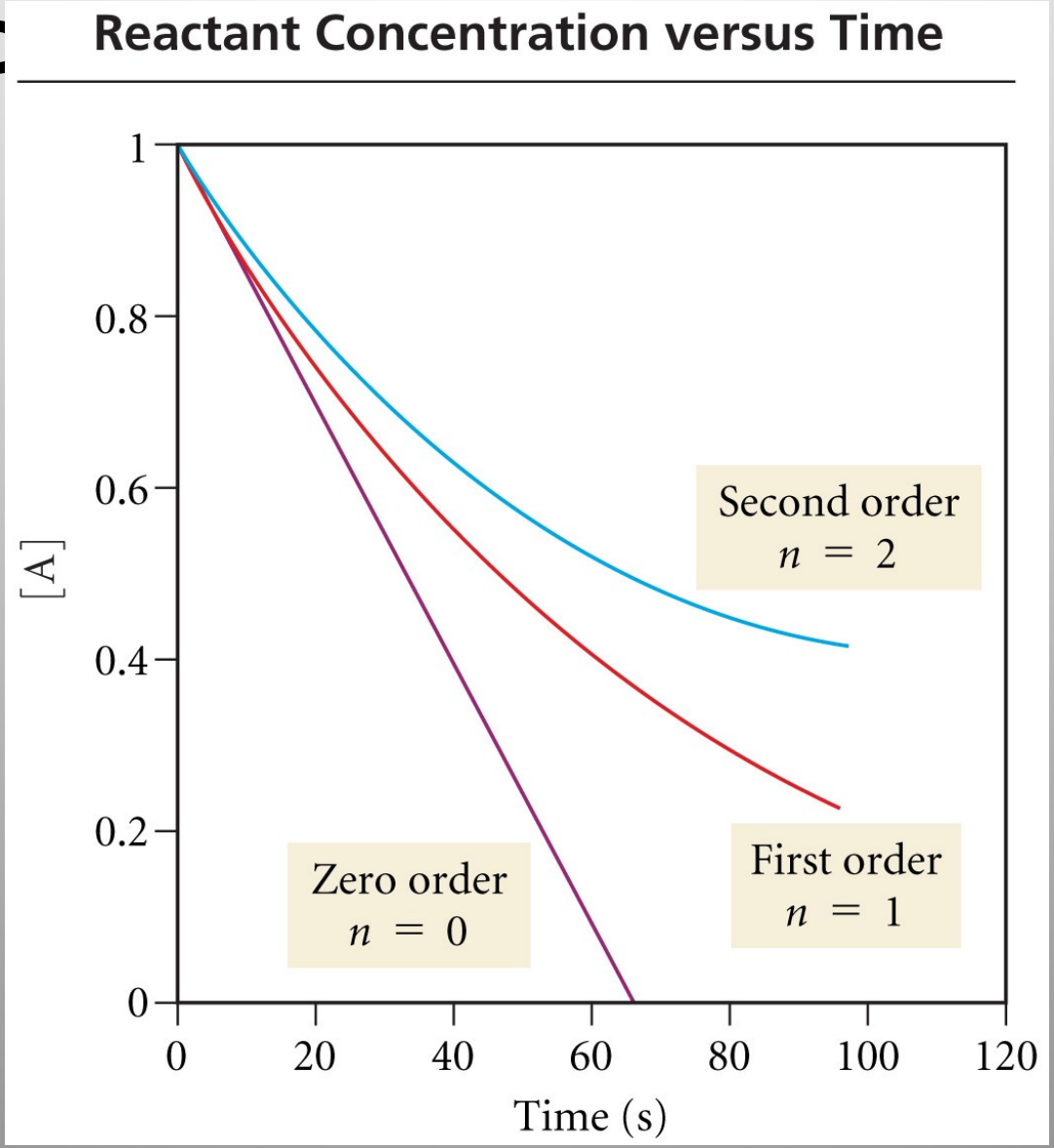
The reaction is
second order with respect to [NO],
first order with respect to $[O_2]$,
and third order overall

Reaction Order

$$\text{Rate} = k[\text{A}]^n[\text{B}]^m$$

- the exponent on each reactant, n and m, in the rate law is called the **order** with respect to that reactant
- the sum of the exponents on the reactants is called the **order of the reaction**
- *k* is called the **rate constant**

[Reactant] vs. Time: A → Produc



Rate Laws Can Only be Determined by Experiment

- Results are represented graphically
  - If graphing [A] vs. time gives a straight line,
    - the exponent on A in rate law is 0
    - the rate constant = negative slope
  - If graphing ln[A] vs. time gives a straight line,
    - the exponent on A in rate law is 1,
    - rate constant = negative slope
  - if graphing 1/[A] vs. time gives a straight line,
    - the exponent on A in rate law is 2,
    - the rate constant = positive slope
- initial rates
  - by comparing effect on the rate from changing the initial concentration of reactants one at a time

Zero Order Reactions

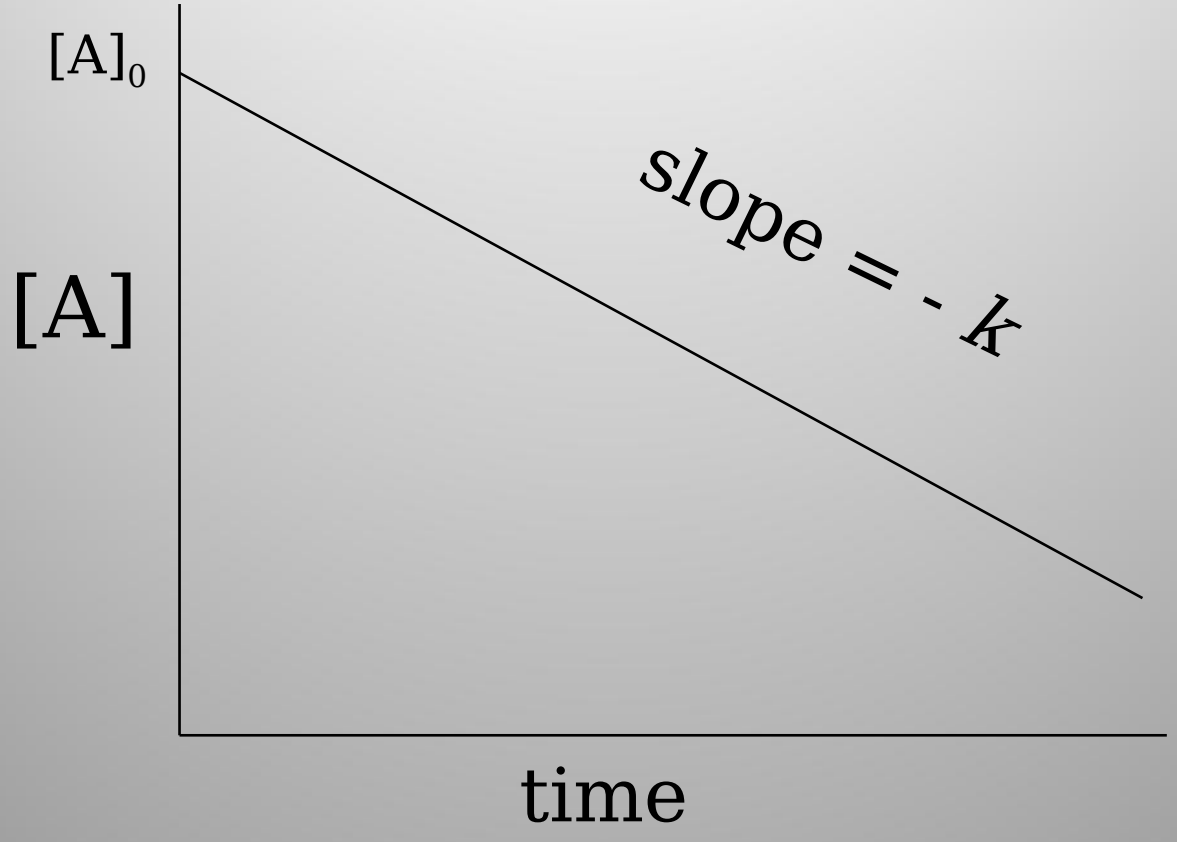
- Rate = $k[A]^0 = k$
  - **constant rate reactions**

- $[A] = -kt + [A]_0$

- graph of [A] vs. time is straight line with **slope = $-k$ and y-intercept = $[A]_0$**

- **when Rate = M/sec, k = M/sec**

Zero Order Reactions

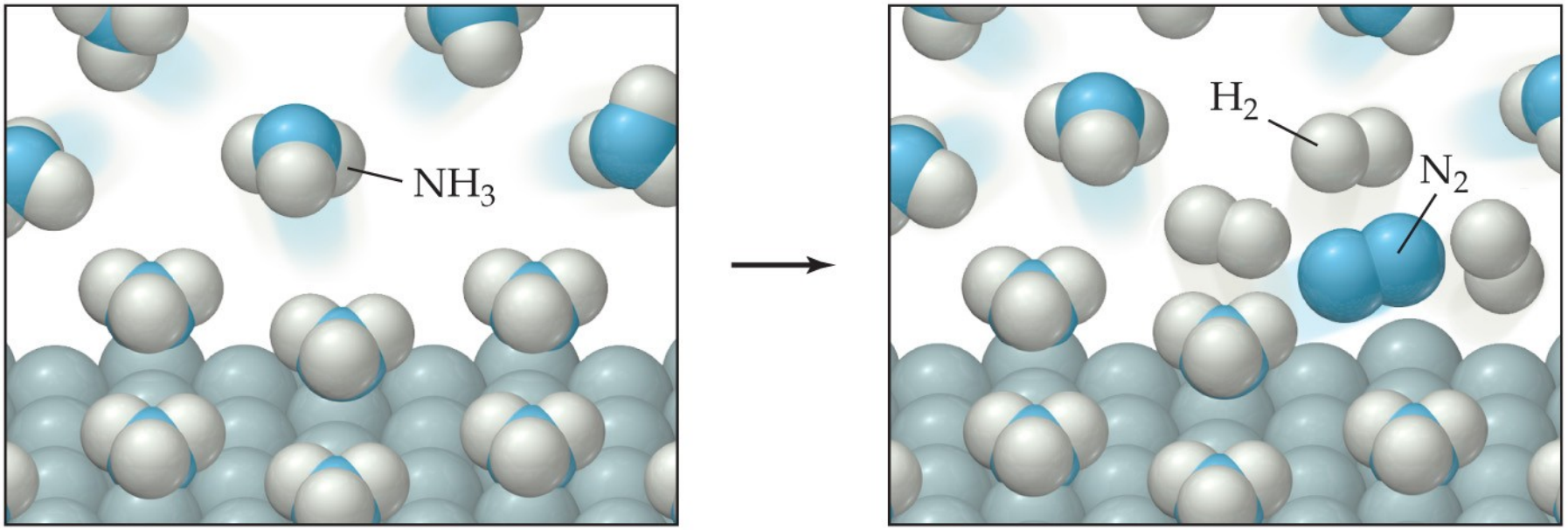


Zero-Order Reactions

rate = $k[NH_3]^0 = k$

Most of the NH_3 molecules are in the gas phase above the surface and are unable to react.

As NH_3 molecules on the surface decompose, they are replaced by molecules from the gas phase, so the number of NH_3 molecules on the surface remains constant.



Because only the NH_3 molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of NH_3.

Half-Life

- the **half-life**, $\mathbf{t_{1/2}}$ **,** of a reaction is the length of time it takes for the concentration of the reactants to fall to ½ its initial value

- the half-life of the reaction depends on the order of the reaction

Half-Life for a zero order rxn

$[A] = -kt + [A]_0$

and at the half-life, the $[A] = ½ [A]_0$

therefore, $kt_{1/2} = [A]_0 - ½ [A]_0$

$kt_{1/2} = ½ [A]_0$

$t_{1/2} = [A]_0 / 2k$

For the reaction A → products,

$$t_{½} = [A_0]/2k$$

First Order Reactions

- Rate = k[A]

- $\ln[A] = -kt + \ln[A]_0$

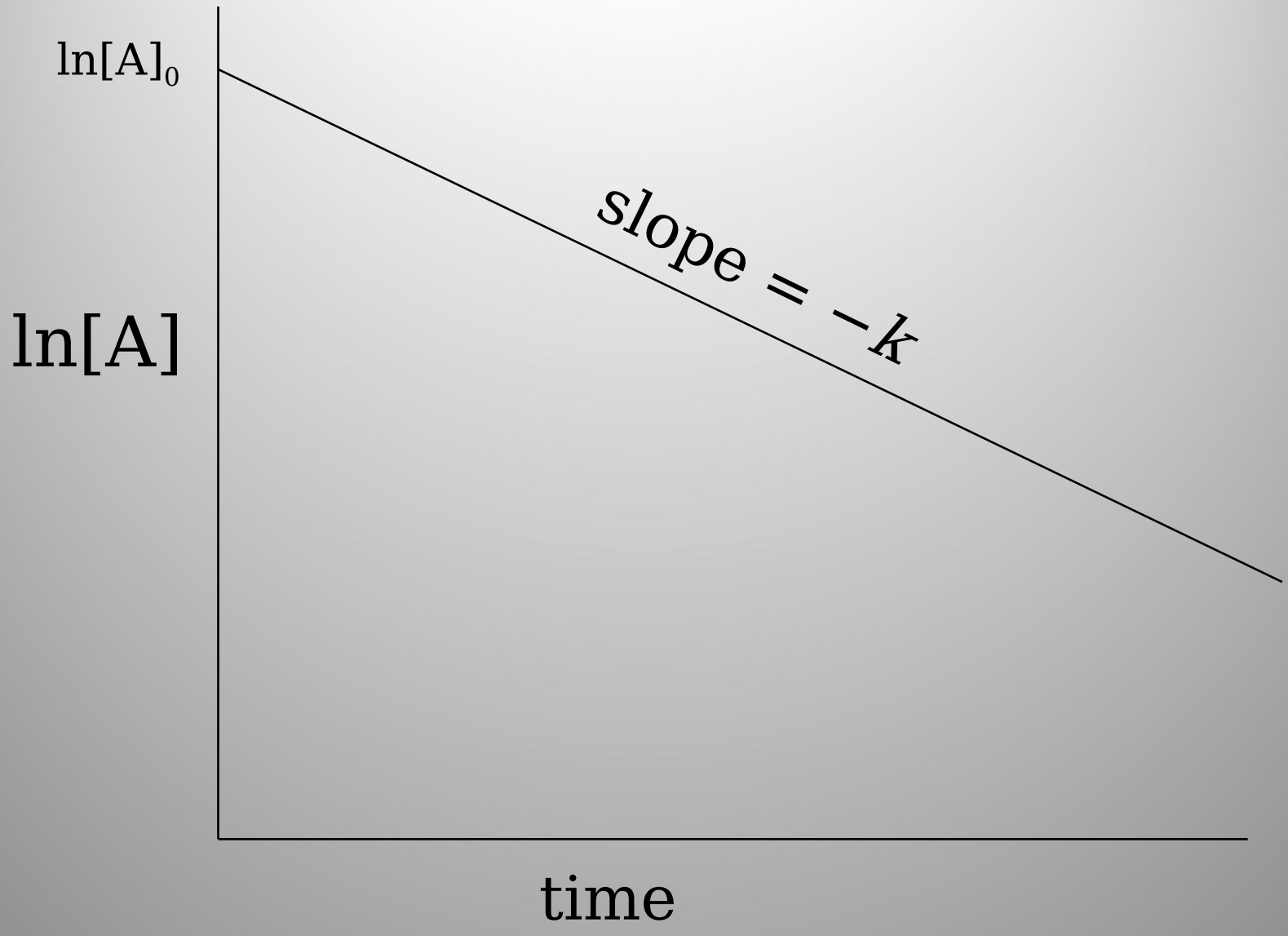
$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$[A]_t$ concentration of A at time t

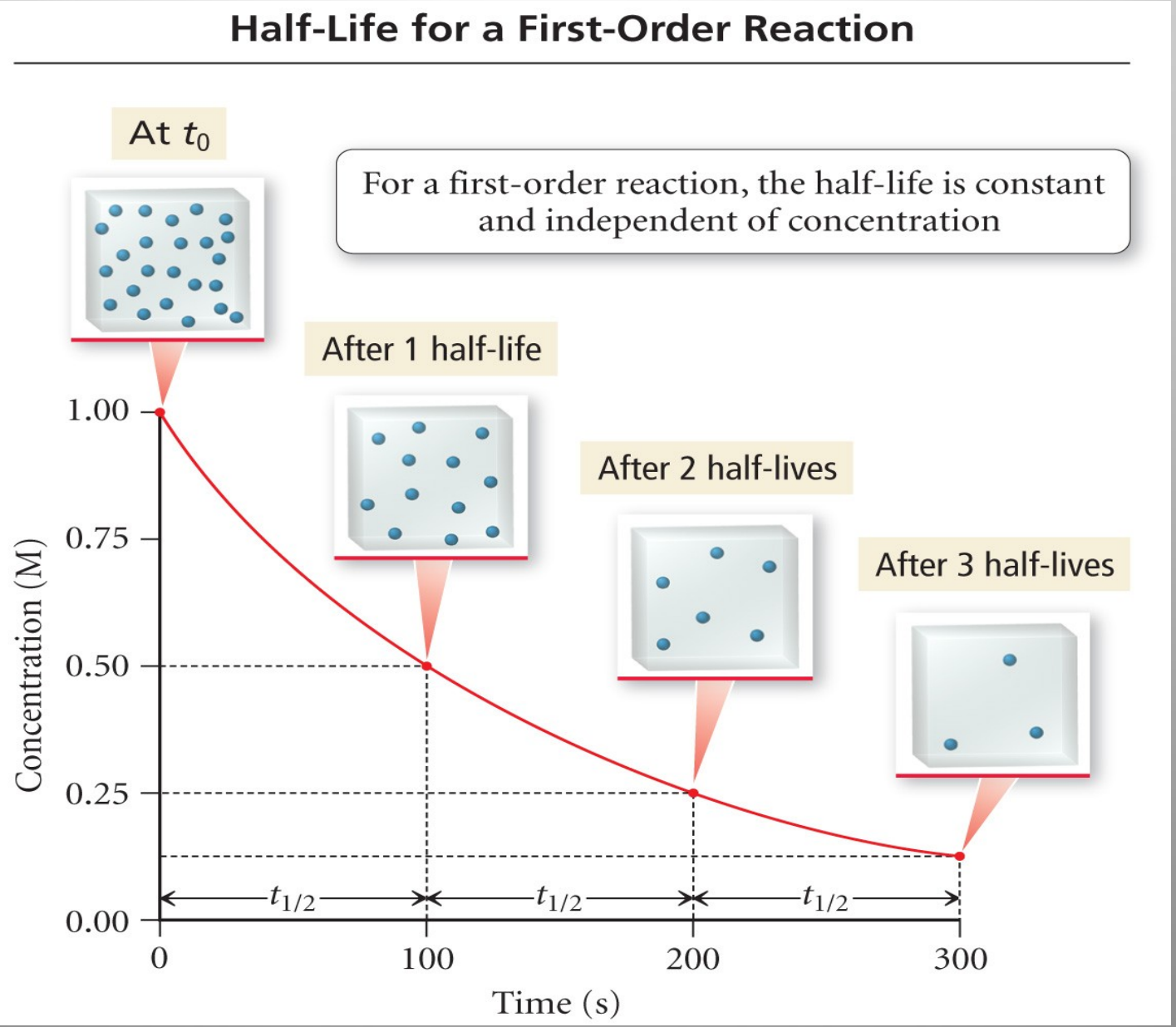
$[A]_0$ initial concentration of A

- graph ln[A] vs. time gives straight line with **slope = $-k$** and **y-intercept = $\ln[A]_0$**
  - used to determine the rate constant

- **Rate = M/sec, k = sec^{-1}**


ln[A]$_0$
ln[A]
slope = $-k$
time

First-Order Rxn Half-Life = Con



Half-Life of a First-Order Reaction

Half-Life: The time required for the reactant concentration to drop to one-half of its initial value.

$$A \longrightarrow \text{product(s)}$$

$$\text{rate} = k[A]$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad \begin{cases} t = t_{1/2} \\ [A]_{t_{1/2}} = \dfrac{[A]_0}{2} \end{cases}$$

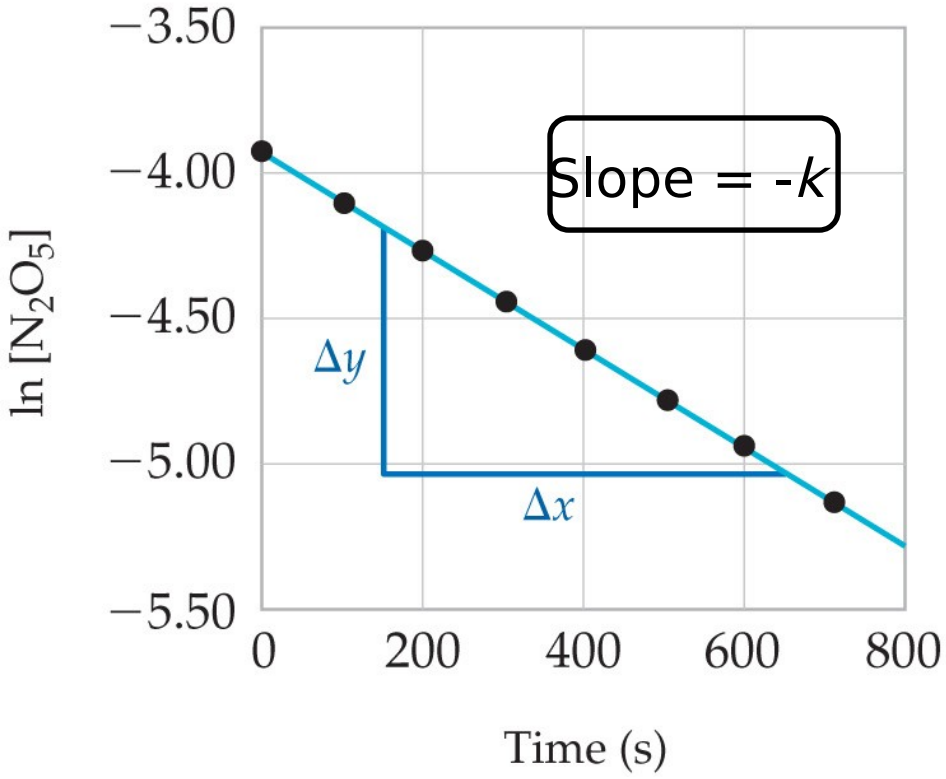
$$\ln\left(\frac{1}{2}\right) = -kt_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k}$$

Integrated Rate Law for a First-Order Reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = k[N_2O_5]$$

Time (s)	$[N_2O_5]$	$\ln [N_2O_5]$
0	0.0200	−3.912
100	0.0169	−4.080
200	0.0142	−4.255
300	0.0120	−4.423
400	0.0101	−4.595
500	0.0086	−4.756
600	0.0072	−4.934
700	0.0061	−5.099



Integrated Rate Law for a First-Order Reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = k[N_2O_5]$$

Calculate the slope:

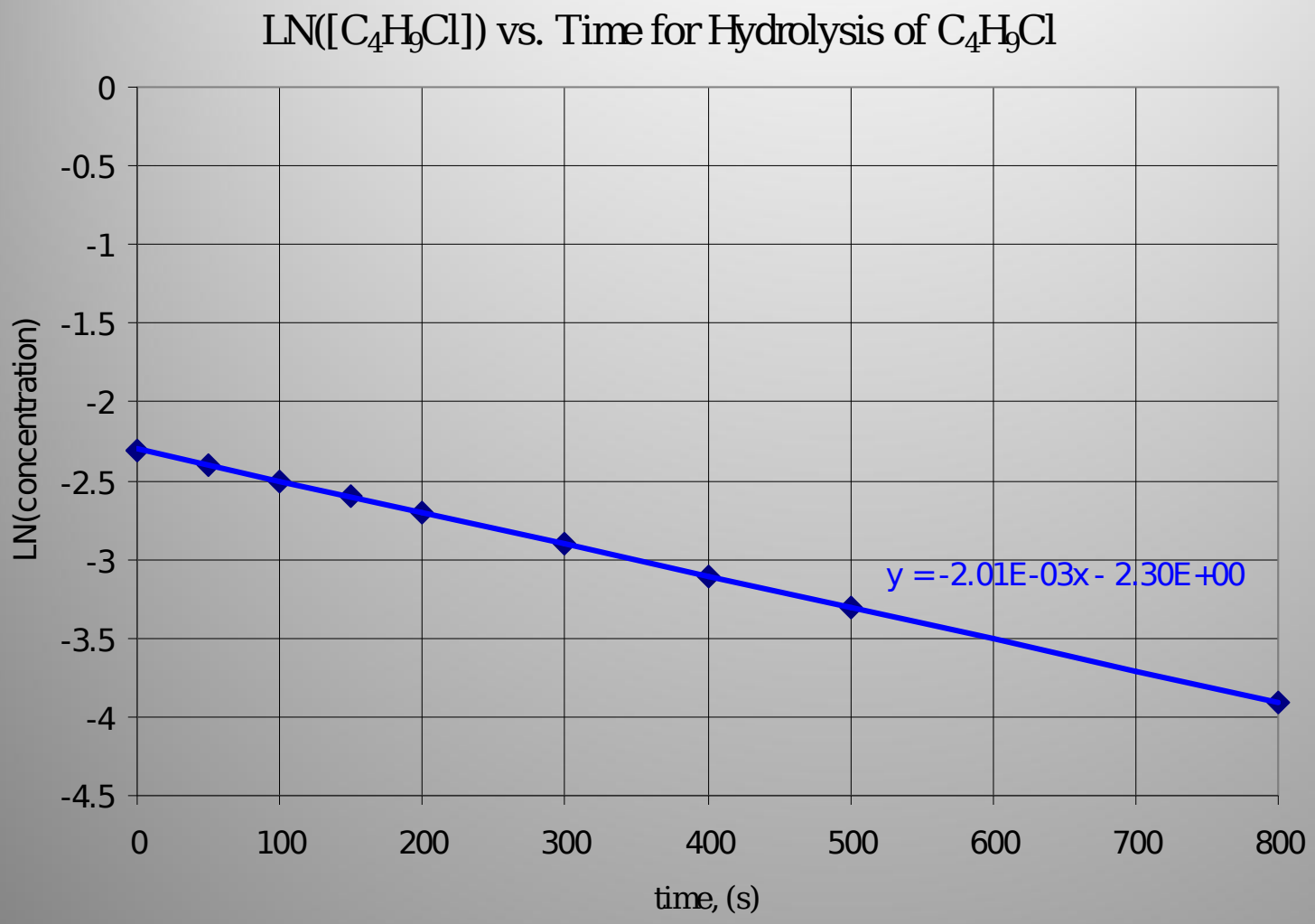
$$\frac{-5.099 - (-3.912)}{(700 - 0)\ \text{s}} = -0.0017 \frac{1}{\text{s}}$$

$$k = 0.0017 \frac{1}{\text{s}}$$

Rate Data for $C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

Time (sec)	$[C_4H_9Cl]$, M
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10000.0	0.0000

$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + 2\ HCl$



slope = -2.01×10^{-3}

$k = 2.01 \times 10^{-3}\ s^{-1}$

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{2.01 \times 10^{-3}\ s^{-1}}$$

$$= 345 s$$

Second Order Reactions

- Rate = $k[A]^2$
- $1/[A] = kt + 1/[A]_0$
- graph 1/[A] vs. time gives straight line with **slope = *k*** and **y-intercept = $1/[A]_0$**
- **Rate = M/sec, $k = M^{-1} \cdot sec^{-1}$**

Calculus can be used to derive an **integrated** rate law.

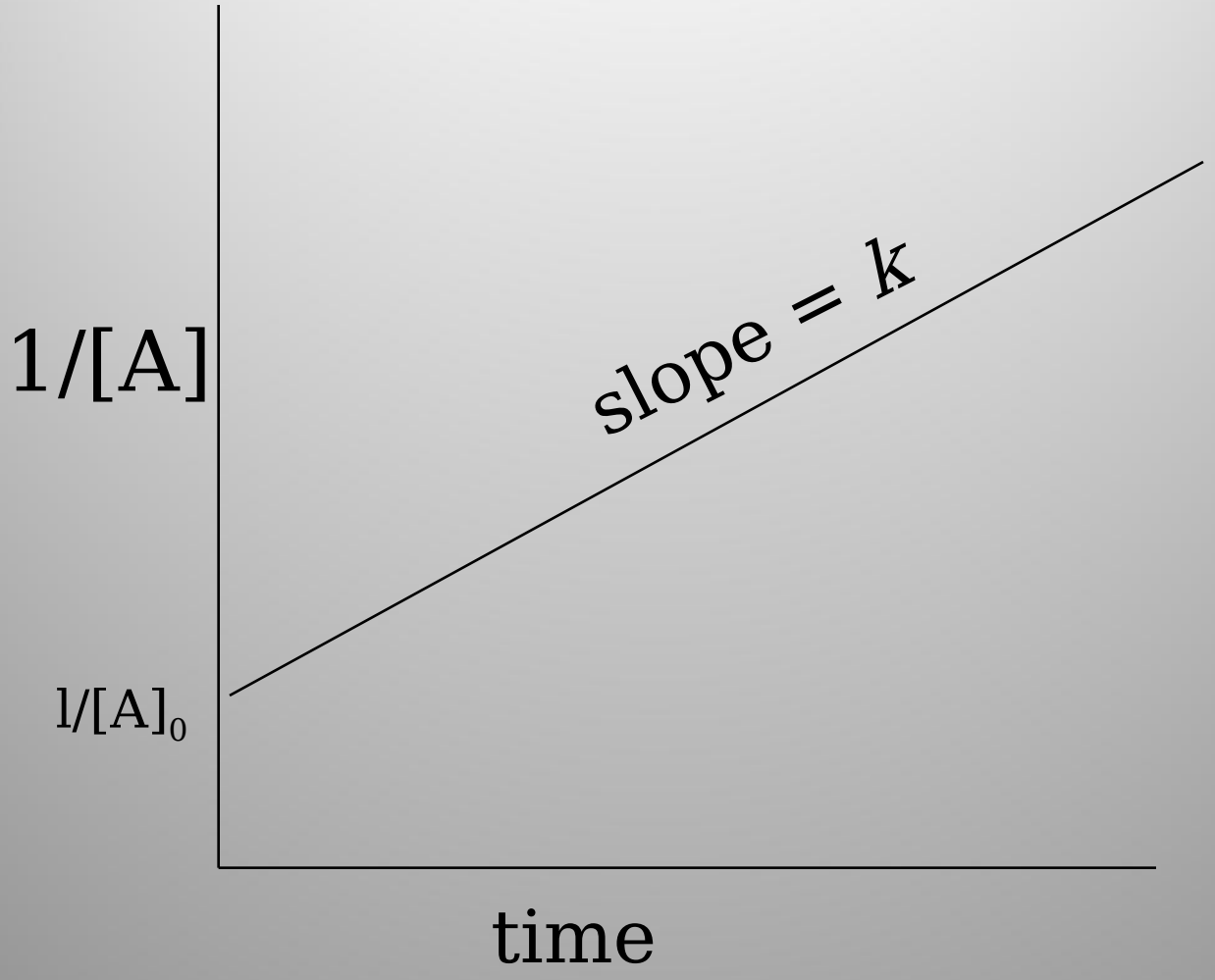
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

$[A]_t$ concentration of A at time t

$[A]_0$ initial concentration of A

Second Order Reactions



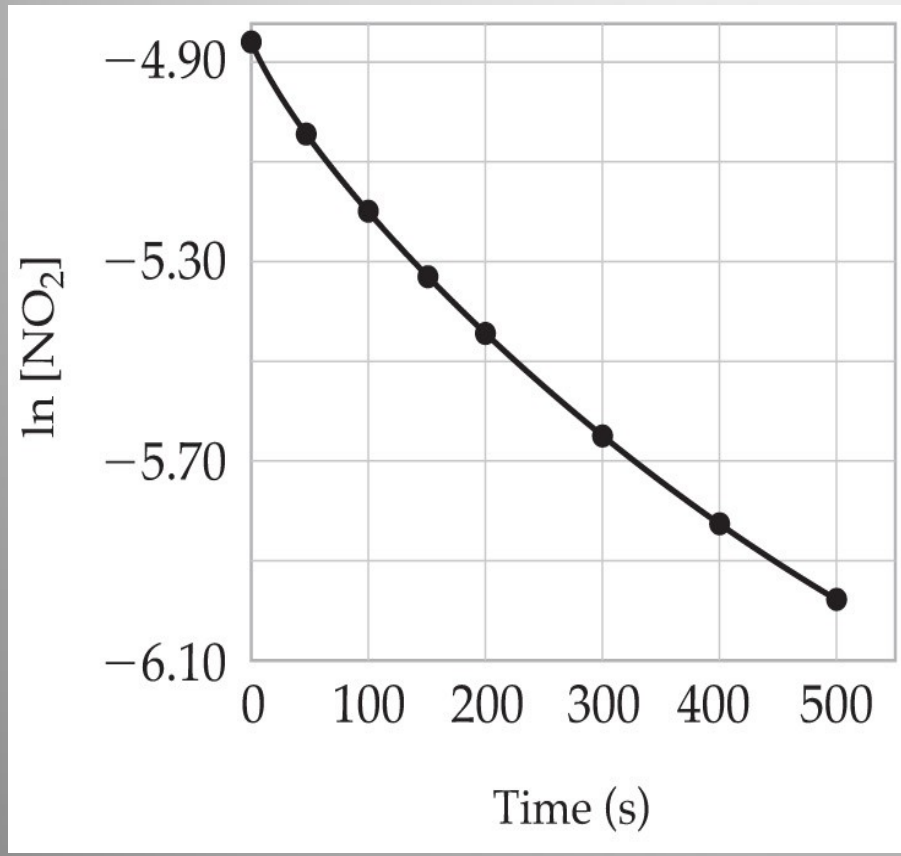
Second-Order Reactions

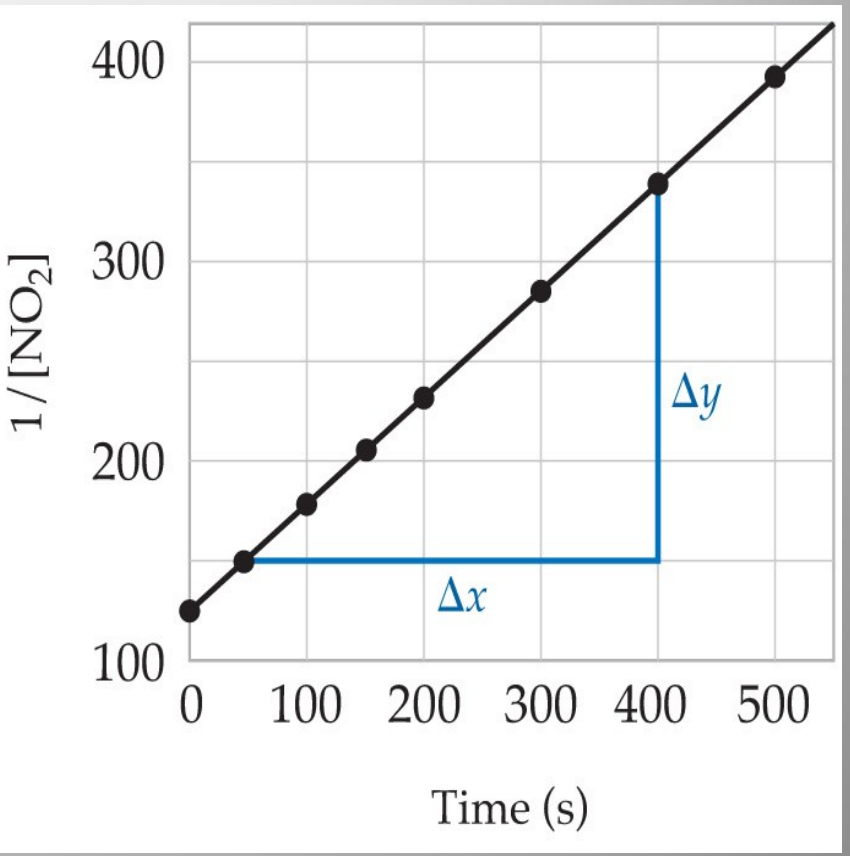
$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

Time (s)	$[NO_2]$	$\ln[NO_2]$	$1/[NO_2]$
0	8.00×10^{-3}	-4.828	125
50	6.58×10^{-3}	-5.024	152
100	5.59×10^{-3}	-5.187	179
150	4.85×10^{-3}	-5.329	206
200	4.29×10^{-3}	-5.451	233
300	3.48×10^{-3}	-5.661	287
400	2.93×10^{-3}	-5.833	341
500	2.53×10^{-3}	-5.980	395

Second-Order Reactions

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$





Second-Order Reactions

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

Calculate the slope:

$$\frac{(395 - 125)\dfrac{1}{M}}{(500 - 0)\ s} = 0.540\frac{1}{M\ s}$$

$$k = 0.540\frac{1}{M\ s}$$

Half-life for Second-Order Rxns

$$A \longrightarrow \text{product(s)}$$

$$\text{rate} = k[A]^2$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\begin{cases} t = t_{1/2} \\ [A]_{t_{1/2}} = \dfrac{[A]_0}{2} \end{cases}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

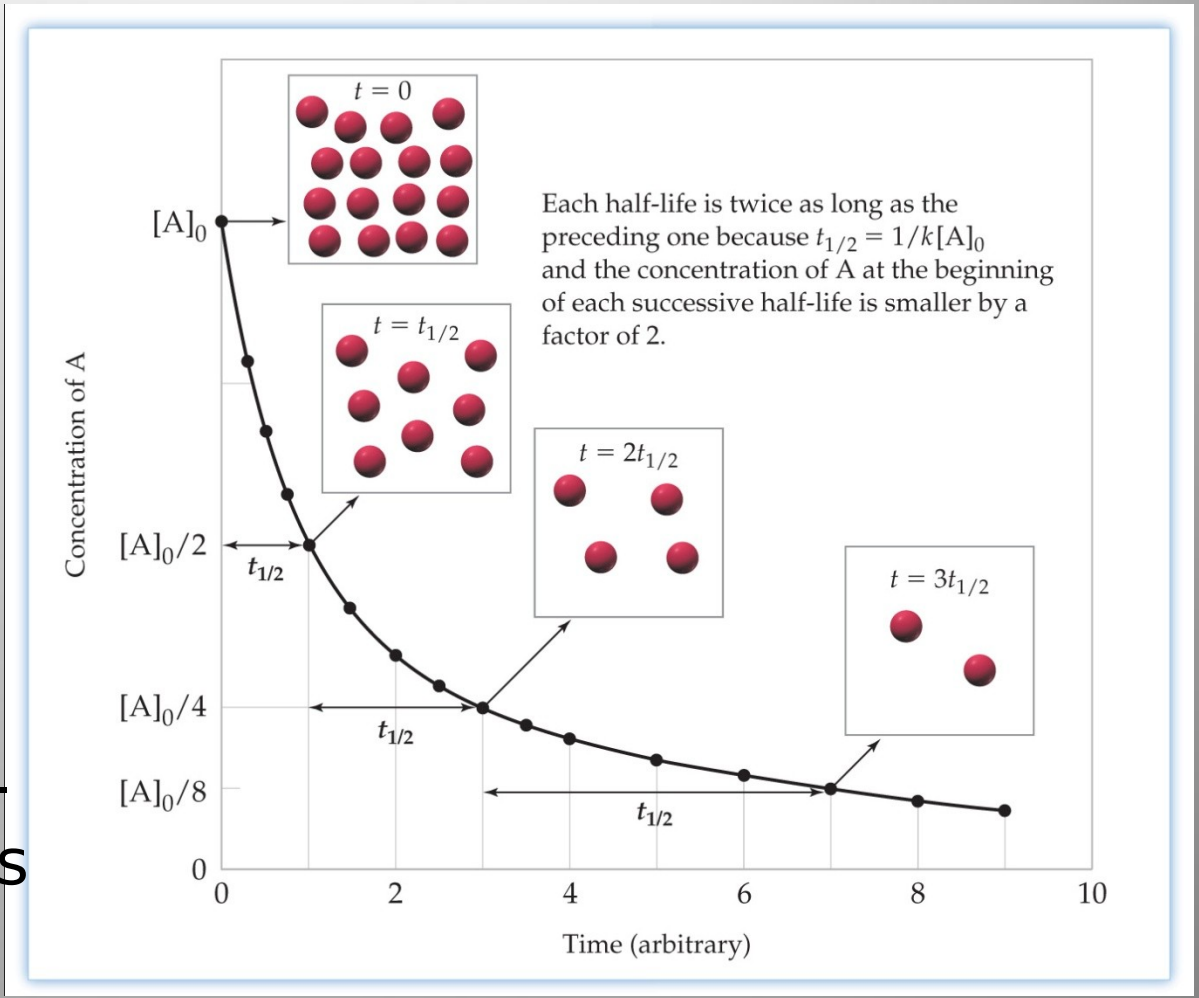
$$t_{1/2} = \frac{1}{k[A]_0}$$

Second-Order Reactions

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, the half-life is dependent on the initial concentration.

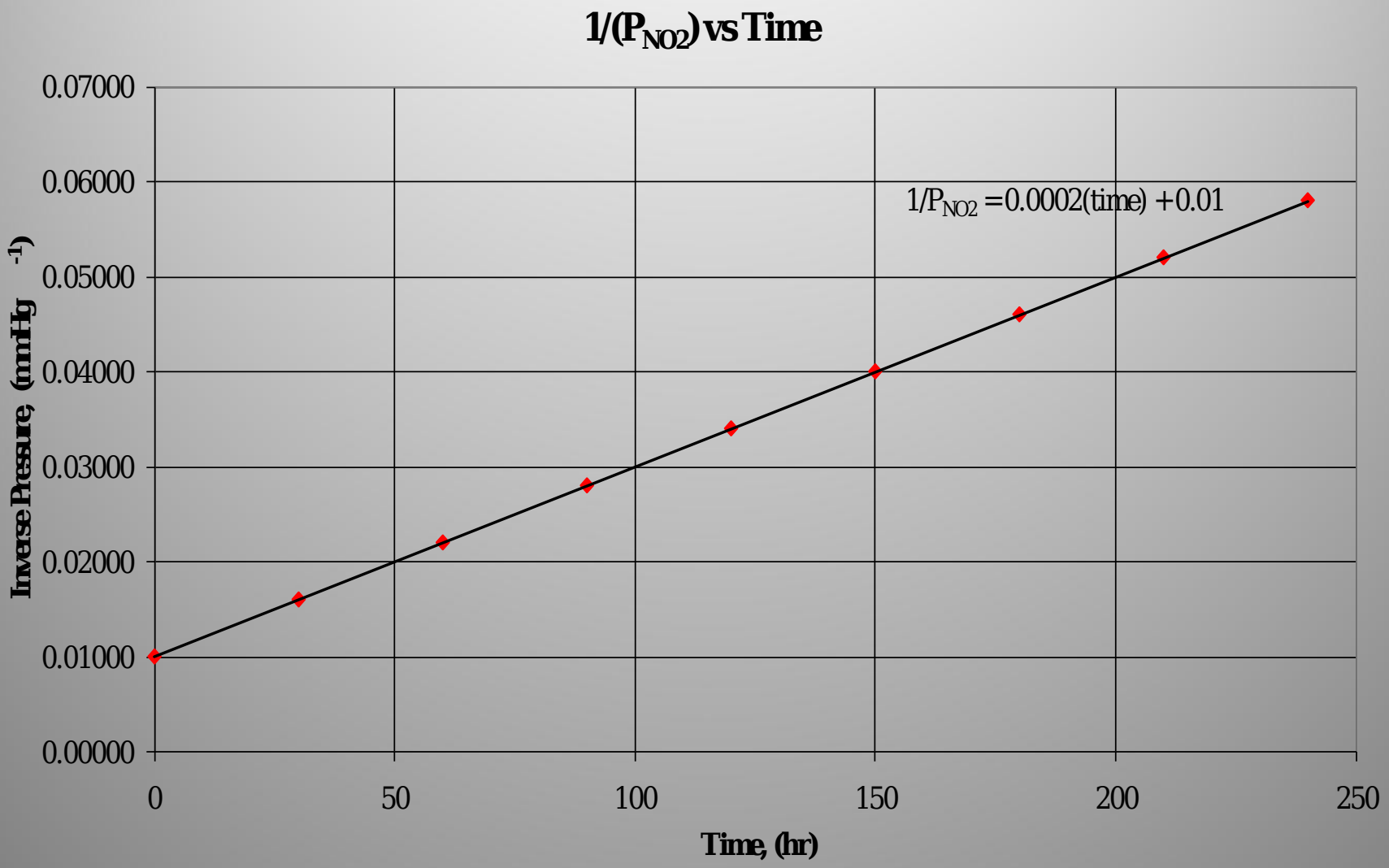
Each successive half-life is twice as long as the preceding one.



Rate Data for: $2\ NO_2 \rightarrow 2\ NO + O_2$

Time (hrs.)	Partial Pressure NO_2, mmHg	$\ln(P_{NO2})$	$1/(P_{NO2})$
0	100.0	4.605	0.01000
30	62.5	4.135	0.01600
60	45.5	3.817	0.02200
90	35.7	3.576	0.02800
120	29.4	3.381	0.03400
150	25.0	3.219	0.04000
180	21.7	3.079	0.04600
210	19.2	2.957	0.05200
240	17.2	2.847	0.05800

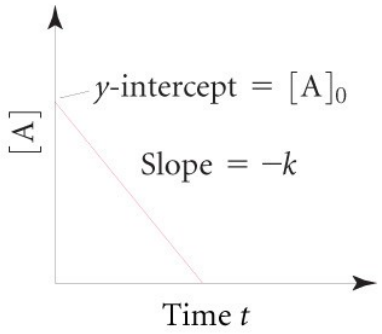
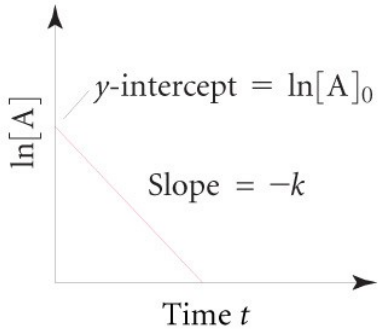
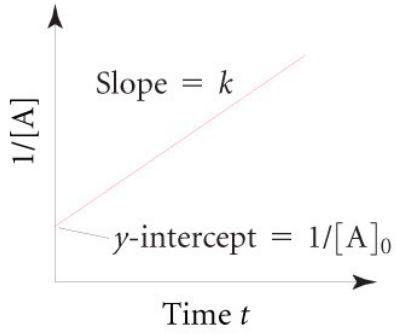
Rate Data Graphs For $2\ NO_2 \rightarrow 2\ NO + O_2$



Rate Laws

Rate Law	Overall Reaction Order	Units for *k*
Rate = k	Zeroth order	M/s or M s^{-1}
Rate = k[A]	First order	1/s or s^{-1}
Rate = k[A][B]	Second order	1/(M • s) or $M^{-1}s^{-1}$
Rate = k[A][B]^2	Third order	1/(M^2 • s) or $M^{-2}s^{-1}$

TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	$\text{Rate} = k[\text{A}]^0$	$\text{M}\cdot\text{s}^{-1}$	$[\text{A}]_t = -kt + [\text{A}]_0$		$t_{1/2} = \frac{[\text{A}]_0}{2k} = \frac{1}{k}\frac{[\text{A}]_0}{2}$
1	$\text{Rate} = k[\text{A}]^1$	s^{-1}	$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$ $\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	$\text{Rate} = k[\text{A}]^2$	$\text{M}^{-1}\text{s}^{-1}$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$		$t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{k}\frac{1}{[\text{A}]_0}$

Logarithms

$$x = b^y$$

is the same as

$$y = \log_b x$$

$X = 10^5$ means $\log_{10} X = 5$

Natural Logarithm Manipulations:

$$\ln(x \cdot y) = \ln(x) + \ln(y)$$

$$\ln(x/y) = \ln(x) - \ln(y)$$

$$\ln(x^n) = n \cdot \ln(x)$$

$$\ln(x) = y \quad x = e^y$$

The reaction $SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$ is first order with a rate constant of 2.90 x 10^{-4} s^{-1} at a given set of conditions. Find the $[SO_2Cl_2]$ at 865 s when $[SO_2Cl_2]_0 = 0.0225$ M

Given:	$[SO_2Cl_2]_0 = 0.0225$ M, t = 865, $k = 2.90 \times 10^{-4}\ s^{-1}$
Find:	
Concept Plan:	$[SO_2Cl_2]_0$, t, k → $[SO_2Cl_2]$
Relationships:	for a 1st order process: $\ln[A] = -kt + \ln[A]_0$
Solution:	$\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0$ $\ln[SO_2Cl_2] = (-2.90 \times 10^{-4}\ s^{-1})(865\ s) + \ln(0.0225)$ $\ln[SO_2Cl_2] = -0.251 - 3.79 = -4.04$ $[SO_2Cl_2] = e^{(-4.04)} = 0.0175$ M
Check:	the new concentration is less than the original, as expected

Initial Rate Method

- another method for determining the order of a reactant is to see the effect on the initial rate of the reaction when the initial concentration of that reactant is changed
  - **for multiple reactants, keep initial concentration of all reactants constant except one**
  - zero order = changing the concentration has no effect on the rate
  - first order = the rate changes by the same factor as the concentration
    - doubling the initial concentration will double the rate
  - second order = the rate changes by the square of the factor the concentration changes
    - doubling the initial concentration will quadruple the rate

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Write a general rate law including all reactants

Examine the data and find two experiments in which the concentration of one reactant changes, but the other

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

$$\text{Rate} = k[NO_2]^n[CO]^m$$

Comparing Expt #1 and Expt #2, the $[NO_2]$ changes but the [CO] does not

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Determine by what factor the concentrations and rates change in these two experiments.

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

$$\frac{[NO_2]_{expt\,2}}{[NO_2]_{expt\,1}} = \frac{0.20\,M}{0.10\,M} = 2 \qquad \frac{Rate_{expt\,2}}{Rate_{expt\,1}} = \frac{0.0082\,M/s}{0.0021\,M/s} \approx 4$$

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Determine to what power the concentration factor must be raised to equal the rate factor.

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

$$\frac{[NO_2]_{expt2}}{[NO_2]_{expt1}} = \frac{0.20M}{0.10M} = 2$$

$$\frac{Rate_{expt2}}{Rate_{expt1}} = \frac{0.0082\ M/s}{0.0021\ M/s} \approx 4$$

$$\left(\frac{[NO_2]_{expt2}}{[NO_2]_{expt1}}\right)^n = \frac{Rate_{expt2}}{Rate_{expt1}}$$

$$2^n = 4$$

$$n = 2$$

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Repeat for the other reactants

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

$$\frac{[CO]_{expt\,3}}{[CO]_{expt\,2}} = \frac{0.20\,M}{0.10\,M} = 2$$

$$\frac{Rate_{expt\,3}}{Rate_{expt\,2}} = \frac{0.0083\,M/s}{0.0082\,M/s} \approx 1$$

$$\left(\frac{[CO]_{expt\,3}}{[CO]_{expt\,2}}\right)^{m} = \frac{Rate_{expt\,3}}{Rate_{expt\,2}}$$

$$2^{m} = 1$$

$$m = 0$$

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

Substitute the exponents into the general rate law to get the rate law for the reaction

$n = 2, m = 0$ $\text{Rate} = k[NO_2]^n[CO]^m$

$\text{Rate} = k[NO_2]^2[CO]^0$ but $[CO]^0 = 1$ ∴

$\text{Rate} = k[NO_2]^2$

Determine the rate law and rate constant for the rxn $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Substitute the concentrations and rate for any experiment into the rate law and solve for *k*

Expt. Number	Initial $[NO_2]$, (M)	Initial [CO], (M)	Initial Rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083
4.	0.40	0.10	0.033

$$\text{Rate} = k[NO_2]^2 \text{ for expt 1}$$

$$0.0021\ \text{M/s} = k(0.10\text{M})^2$$

$$k = \frac{0.0021\ \text{M/s}}{0.01\text{M}^2} = 0.21\text{M}^{-1} \bullet \text{s}^{-1}$$

Determine the rate law and rate constant for the reaction $NH_4^{+1} + NO_2^{-1} \rightarrow N_2 + 2\ H_2O$ given the data below.

Expt. No.	Initial $[NH_4^+]$, M	Initial $[NO_2^-]$, M	Initial Rate, $(x\ 10^{-7})$, M/s
1	0.0200	0.200	10.8
2	0.0600	0.200	32.3
3	0.200	0.0202	10.8
4	0.200	0.0404	21.6

Determine the rate law and rate constant for the reaction $NH_4^{+1} + NO_2^{-1} \rightarrow N_2 + 2\ H_2O$ given the data below.

Expt. No.	Initial $[NH_4^+]$, M	Initial $[NO_2^-]$, M	Initial Rate, (x 10^{-7}), M/s
1	0.0200	0.200	10.8
2	0.0600	0.200	32.3
3	0.200	0.0202	10.8
4	0.200	0.0404	21.6

For $[NH_4^+]$, $\frac{\text{Expt 2}}{\text{Expt 1}} = \frac{0.0600}{0.0200} = 3$

Rate, $\frac{\text{Expt 2}}{\text{Expt 1}} = \frac{32.3 \times 10^{-7}}{10.8 \times 10^{-7}} = 3$

Rate Factor $= [NH_4^+]^n\ 3 = 3^n$

$\therefore n = 1$, first order

$$\text{Rate} = k[NH_4^+]^n[NO_2^-]^m$$

Determine the rate law and rate constant for the reaction $NH_4^{+1} + NO_2^{-1} \rightarrow N_2 + 2\ H_2O$ given the data below.

Expt. No.	Initial $[NH_4^+]$, M	Initial $[NO_2^-]$, M	Initial Rate, (x 10^{-7}), M/s
1	0.0200	0.200	10.8
2	0.0600	0.200	32.3
3	0.200	0.0202	10.8
4	0.200	0.0404	21.6

For $[NO_2^-]$, $\frac{\text{Expt 4}}{\text{Expt 3}} = \frac{0.0404}{0.0202} = 2$

Rate, $\frac{\text{Expt 4}}{\text{Expt 3}} = \frac{21.6 \times 10^{-7}}{10.8 \times 10^{-7}} = 2$

$\text{Rate} = k[NH_4^+]^n[NO_2^-]^m$

$\text{Rate Factor} = [NO_2^-]^m \quad 2 = 2^m$

$\therefore m = 1$, first order

Determine the rate law and rate constant for the reaction $NH_4^{+1} + NO_2^{-1} \rightarrow N_2 + 2\ H_2O$ given the data below.

$$\text{Rate} = k[NH_4^+]^n[NO_2^-]^m$$

Both reactants are first order, ∴ Rate = $k[NH_4^+][NO_2^-]$

$$\text{Rate} = k[NH_4^+][NO_2^-] \text{ for expt 1}$$

$$10.8\times10^{-7}\ \text{M/s} = k(0.0200\ \text{M})(0.200\ \text{M})$$

$$k = \frac{10.8\times10^{-7}\ \text{M/s}}{4.00\times10^{-3}\ \text{M}^2} = 2.70\times10^{-4}\ \text{M}^{-1}\bullet\text{s}^{-1}$$

The Effect of Temperature on Rate

- changing the temperature changes the rate constant of the rate law
- Svante Arrhenius investigated this relationship and showed that:

$$k = A\left(e^{\frac{-E_a}{RT}}\right)$$

A is a factor called the **frequency facto**

A = pZ

- p = fraction collisions with proper orientation
- Z = Constant related to collision frequency

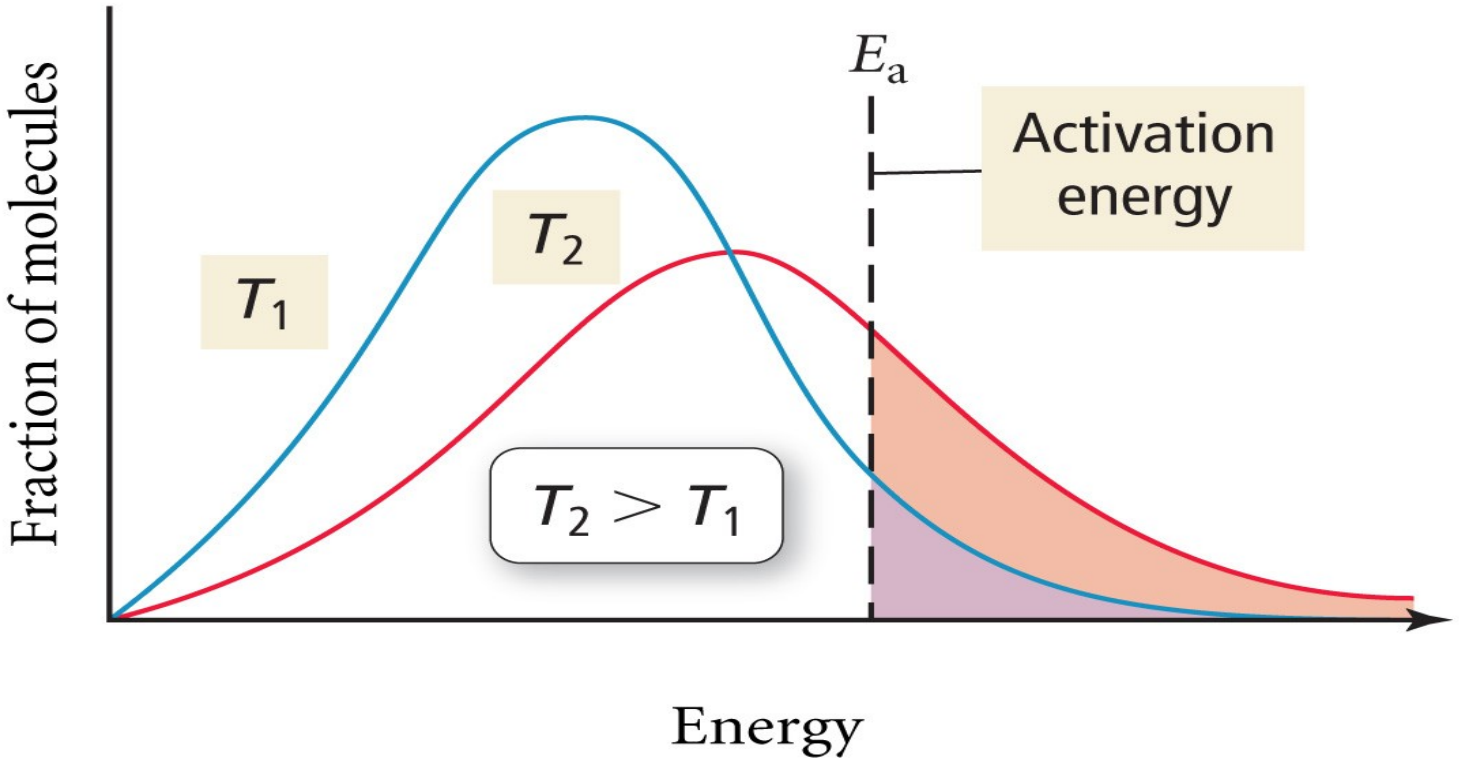
where T is the temperature in kelvins

R is the gas constant in energy units, 8.314 J/(mol•K)

E_a is the **activation energy**, the extra energy needed to start the molecules reacting

Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



Magnesium is inert in cold water.

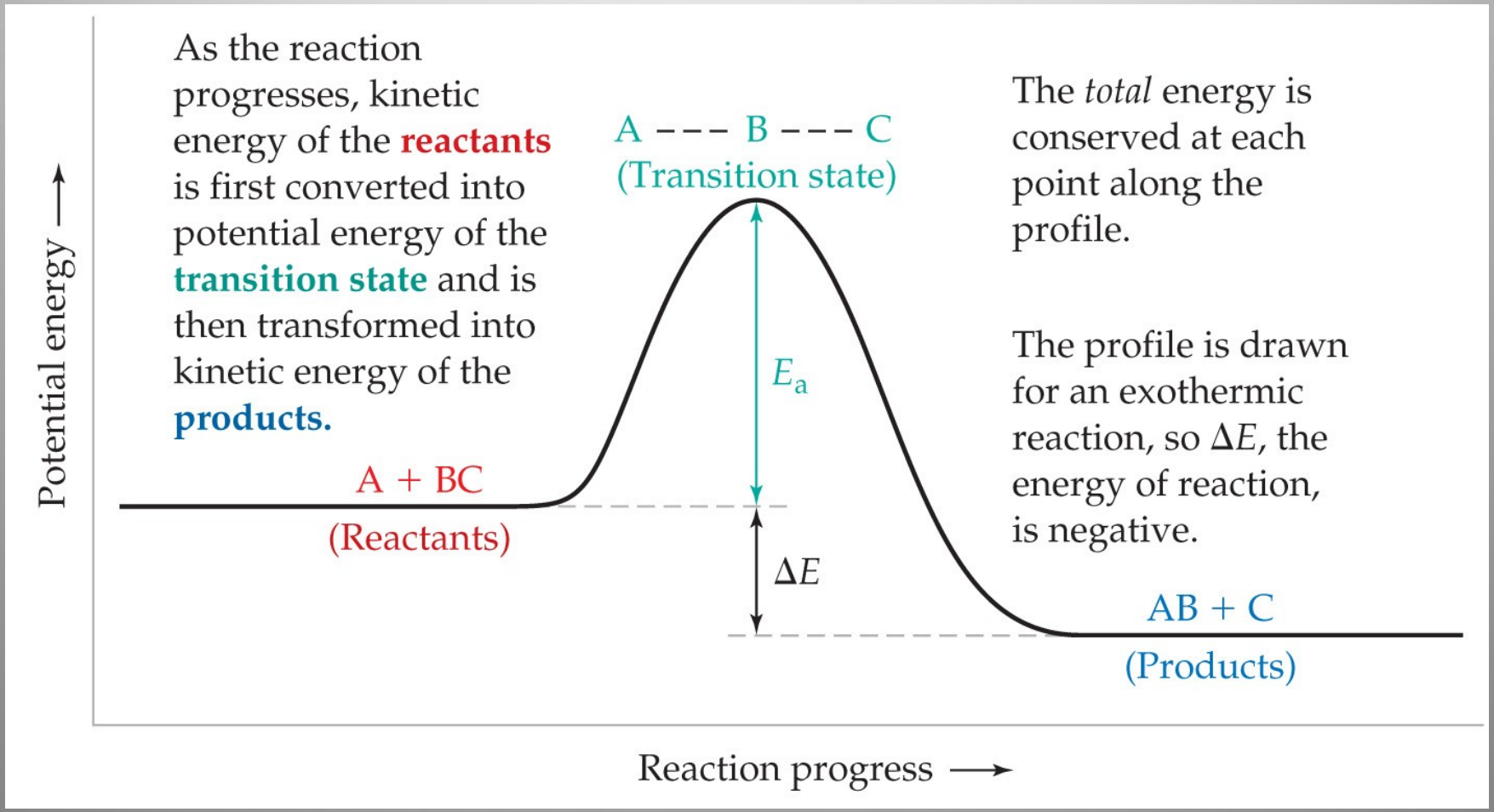
Magnesium reacts in hot water.

$$Mg(s) + 2\,H_2O(l) \longrightarrow Mg^{2+}(aq) + 2\,OH^-(aq) + H_2(g)$$

The formation of bubbles of gas and the pink color of phenolphthalein, which indicates an alkaline solution, provide evidence of the reaction.

The Arrhenius Equation

Transition State: The configuration of atoms at the maximum in the potential energy profile. This is also called the activated complex.


As the reaction progresses, kinetic energy of the reactants is first converted into potential energy of the transition state and is then transformed into kinetic energy of the products.
A --- B --- C
(Transition state)
The total energy is conserved at each point along the profile.
The profile is drawn for an exothermic reaction, so ΔE, the energy of reaction, is negative.
Potential energy
E_a
A + BC
(Reactants)
ΔE
AB + C
(Products)
Reaction progress

Activation Energy and the Activated Complex

- energy barrier to the reaction
- amount of energy needed to convert reactants into the **activated complex**
  - aka transition state
- the activated complex is a chemical species with partially broken and partially formed bonds
  - always very high in energy because partial bonds

Given $k = A\left(e^{\frac{-E_a}{RT}}\right) \longrightarrow \frac{k}{A} = \left(e^{\frac{-E_a}{RT}}\right)$

Recall we said that if $x = e^y$

Then $\ln(x) = y$ $\ln(x/y) = \ln(x) - \ln(y)$

$$\ln(k/A) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) \longrightarrow \ln(k) - \ln(A) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right)$$

$$\longrightarrow \ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

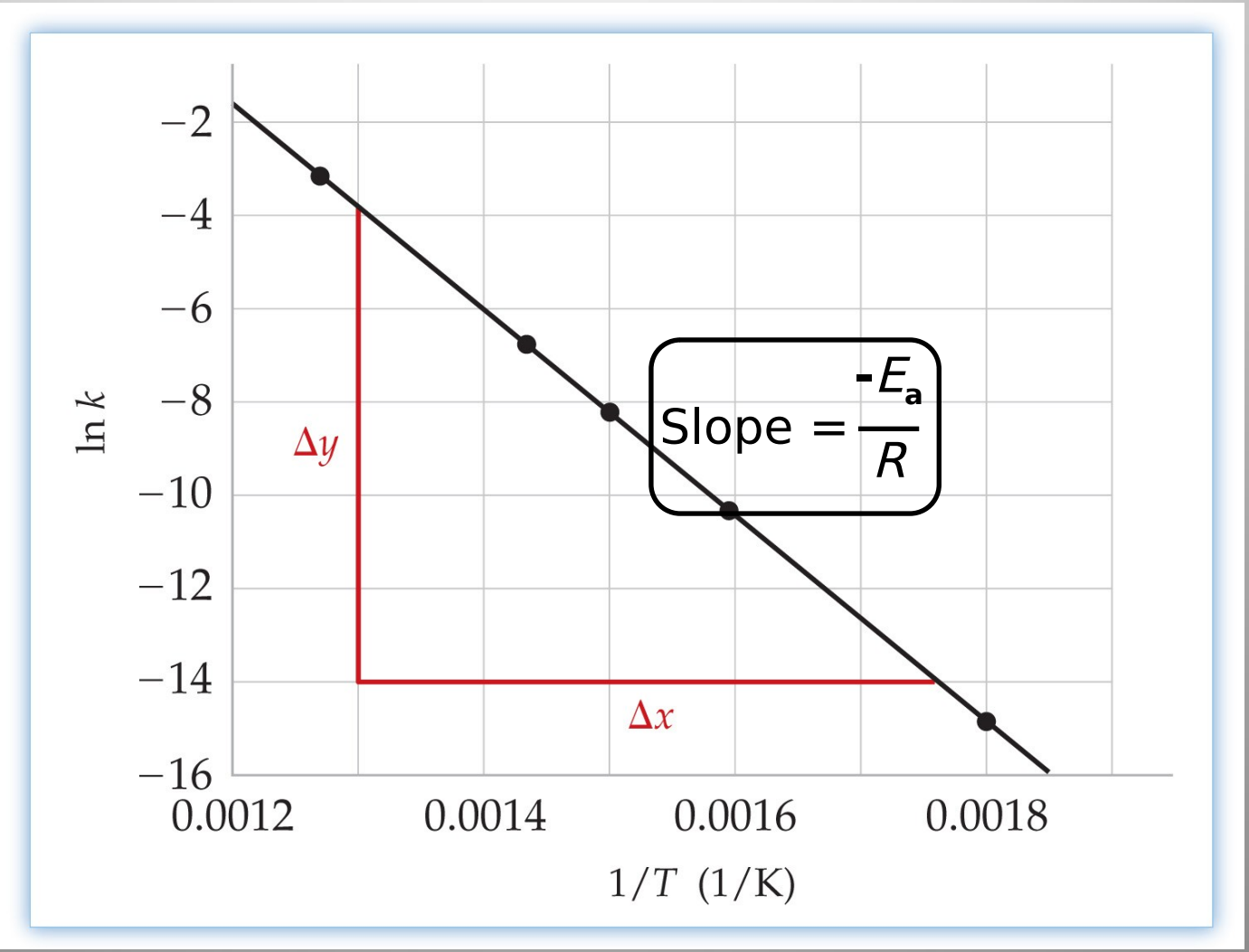
Using the Arrhenius Equation

$$\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

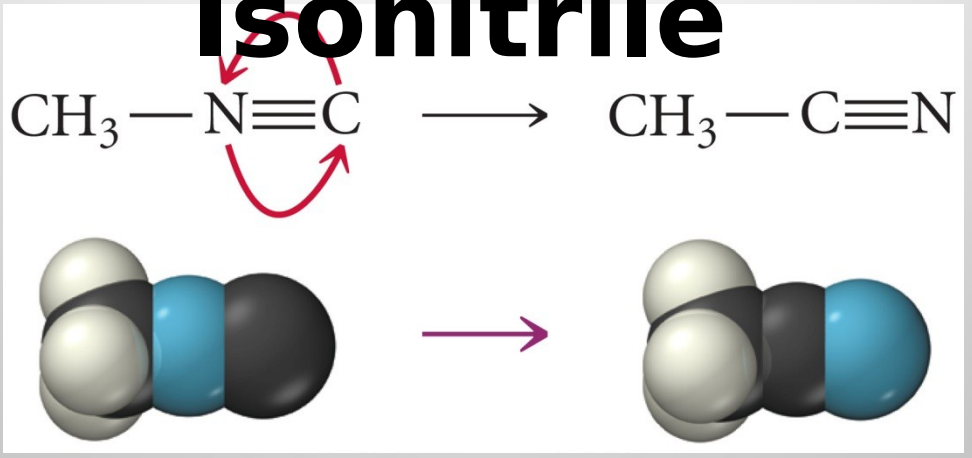
t (°C)	T (K)	k (M^{-1} s^{-1})	$1/T$ (1/K)	ln$k$
283	556	3.52×10^{-7}	0.001 80	-14.860
356	629	3.02×10^{-5}	0.001 59	-10.408
393	666	2.19×10^{-4}	0.001 50	-8.426
427	700	1.16×10^{-3}	0.001 43	-6.759
508	781	3.95×10^{-2}	0.001 28	-3.231

Using the Arrhenius Equation

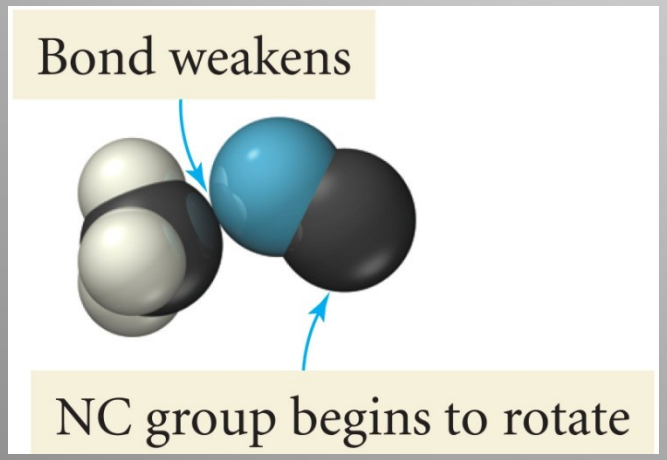
$$\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$



Isomerization of Methyl Isonitrile

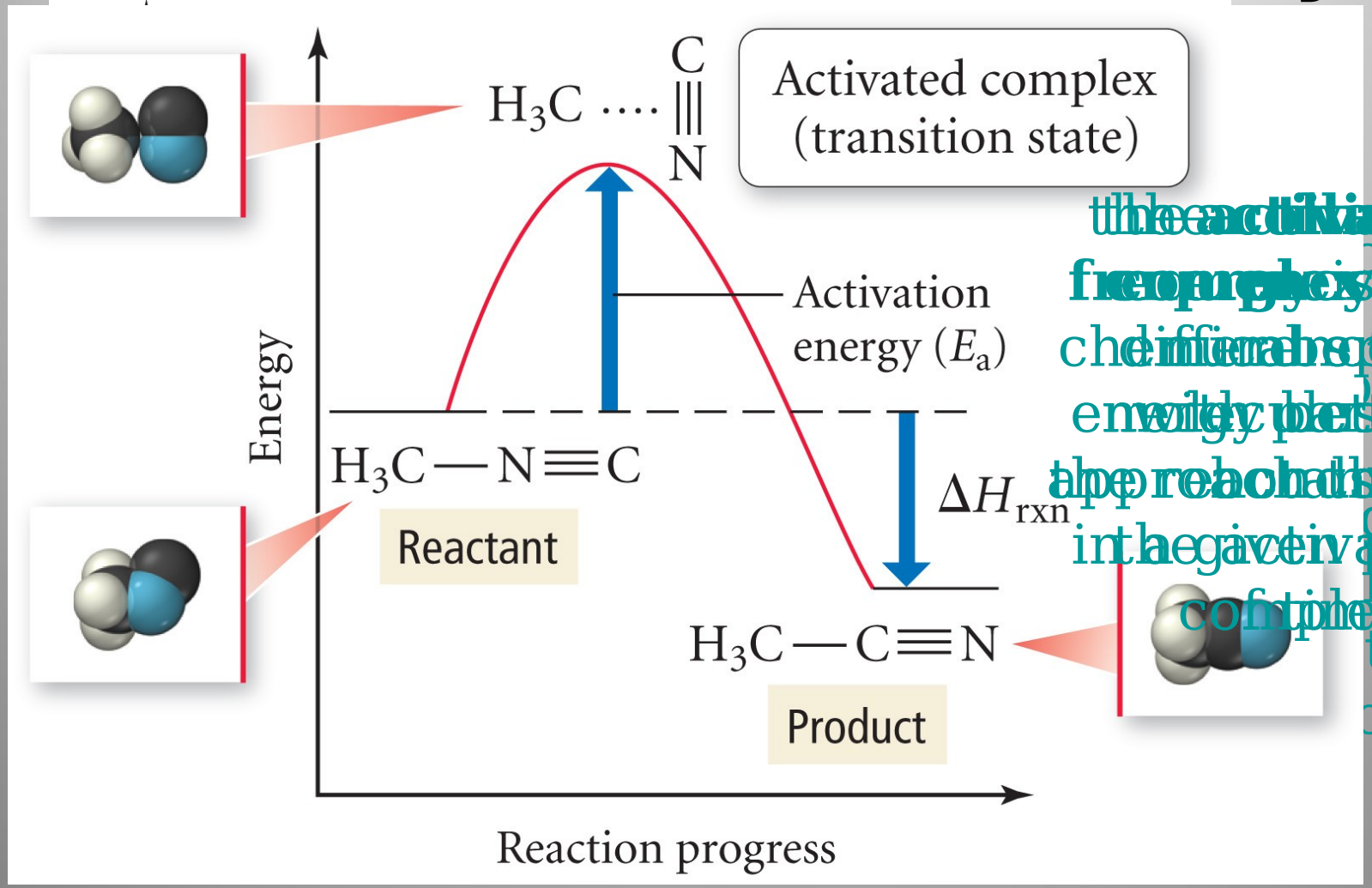


methyl isonitrile rearranges to acetonitrile



in order for the reaction to occur, the H_3C-N bond must break; and a new H_3C-C bond form

Energy Profile for the Isomerization of Methyl



The Arrhenius Equation: The Exponential Factor

- the exponential factor in the Arrhenius equation is a number between 0 and 1
- it represents the fraction of reactant molecules with sufficient energy so they can make it over the energy barrier
  - the higher the energy barrier (larger activation energy), the fewer molecules that have sufficient energy to overcome it
- that extra energy comes from converting the kinetic energy of motion to potential energy in the molecule when the molecules collide
  - increasing the temperature increases the average kinetic energy of the molecules
  - therefore, increasing the temperature will increase the number of molecules with sufficient energy to overcome the energy barrier
  - therefore increasing the temperature will increase the reaction rate

The Arrhenius Equation can be algebraically solved to give the following form:

$$\ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

this equation is in the form $y = mx + b$ where $y = \ln(k)$ and $x = (1/T)$

a graph of $\ln(k)$ vs. $(1/T)$ is a straight line with

Slope = $-E_a$ (in Joules)/8.314 J/mol•K

$\therefore E_a$ (in Joules) = (-8.314 J/mol•K)•(slope of the line)

and the y-intercept is ln(A)

$\ln(x) = y \quad x = e^y \longrightarrow \ln(A) = y \quad A = e^y$

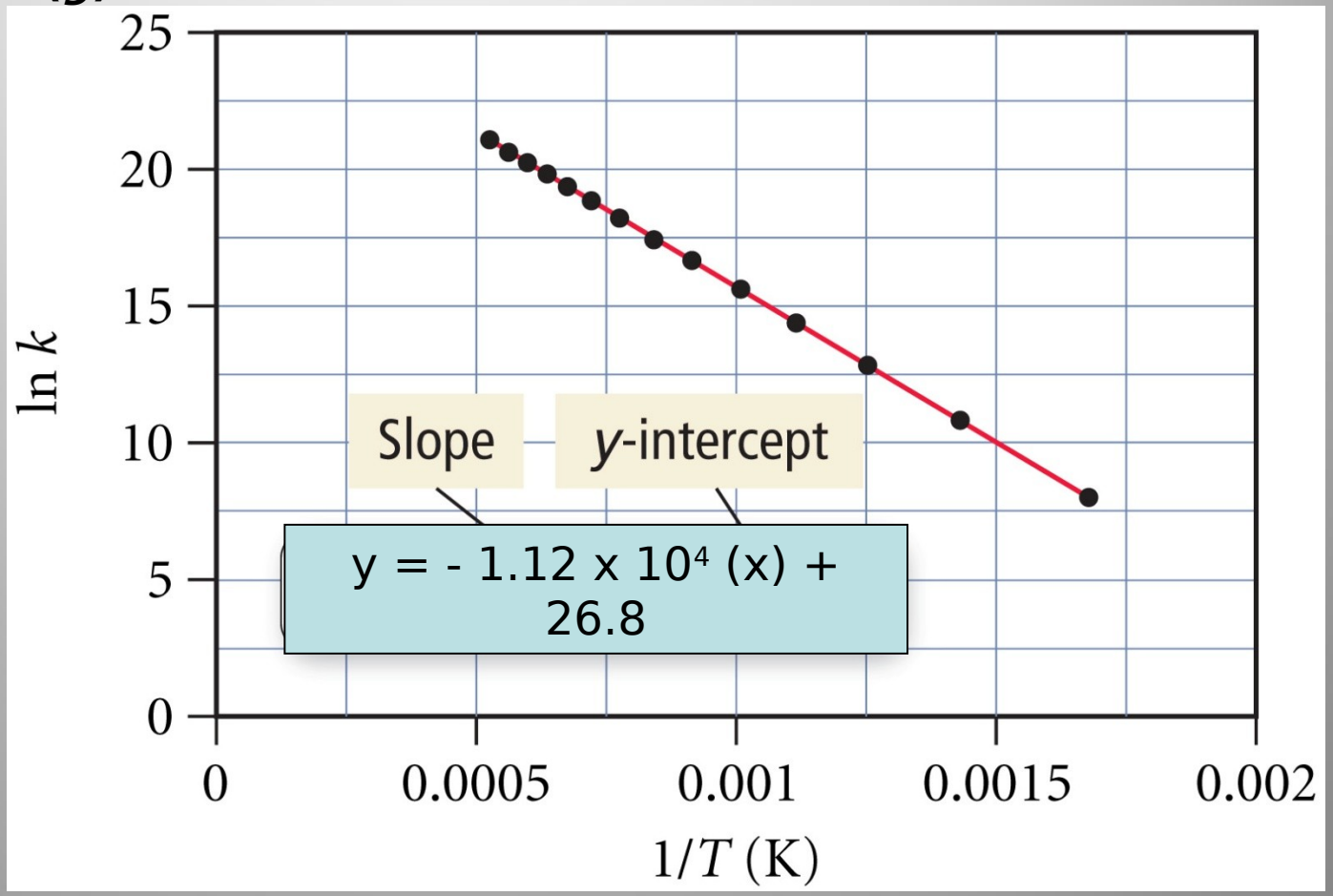
A (unit is the same as k) = $e^{y\text{-intercept}}$

Determine the activation energy and frequency factor for the reaction $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ given the following data:

Temp, K	*k*, $M^{-1} \cdot s^{-1}$	Temp, K	*k*, $M^{-1} \cdot s^{-1}$
600	3.37×10^{3}	1300	7.83×10^{7}
700	4.83×10^{4}	1400	1.45×10^{8}
800	3.58×10^{5}	1500	2.46×10^{8}
900	1.70×10^{6}	1600	3.93×10^{8}
1000	5.90×10^{6}	1700	5.93×10^{8}
1100	1.63×10^{7}	1800	8.55×10^{8}
1200	3.81×10^{7}	1900	1.19×10^{9}

Determine the activation energy and frequency factor for the reaction $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ given the following data:

use a spreadsheet to graph ln(k) vs. (1/T)



Determine the activation energy and frequency factor for the reaction $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ given the following data:

$E_a =$ *slope*$\bullet(-R)$
solve for E_a

$$E_a = \left(-1.12\times10^{4}\ \text{K}\right)\left(-8.314\ \frac{\text{J}}{\text{mol}\bullet\text{K}}\right)$$

$$E_a = 9.31\times10^{4}\ \frac{\text{J}}{\text{mol}} = 931\ \frac{\text{kJ}}{\text{mol}}$$

$A = e^{y\text{-intercept}}$
solve for A

$$A = e^{26.8} = 4.36\times10^{11}$$

$$A = 4.36\times10^{11}\ \text{M}^{-1}\bullet\text{s}^{-1}$$

Arrhenius Equation: Two-Point Form

- if you only have two (T,*k*) data points, the following forms of the Arrhenius Equation can be used:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{(R)\ln\frac{k_1}{k_2}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{(R)\ln\frac{k_1}{k_2}}{\frac{T_1 - T_2}{(T_1)(T_2)}} = \frac{(R)(T_1)(T_2)\ln\frac{k_1}{k_2}}{(T_1 - T_2)}$$

The reaction $NO_{2(g)} + CO_{(g)} \rightarrow CO_{2(g)} + NO_{(g)}$ has a rate constant of 2.57 $M^{-1}\cdot s^{-1}$ at 701 K and 567 $M^{-1}\cdot s^{-1}$ at 895 K. Find the activation energy in kJ/mol.

Given:	$T_1 = 701$ K, $k_1 = 2.57\ M^{-1}\cdot s^{-1}$, $T_2 = 895$ K, $k_2 = 567\ M^{-1}\cdot s^{-1}$
Find:	E_a, kJ/mol
Concept Plan:	$T_1, k_1, T_2, k_2 \rightarrow E_a$ $\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Relationships/ Solutions:	$\ln\left(\frac{567\ M^{-1}\cdot s^{-1}}{2.57\ M^{-1}\cdot s^{-1}}\right) = \frac{-E_a}{8.314\ \frac{J}{mol\cdot K}}\left(\frac{1}{895\text{K}} - \frac{1}{701\text{K}}\right)$ $5.3965 = \frac{-E_a}{8.314\ \frac{J}{mol\cdot K}}(-3.092\times10^{-4}\ K^{-1})$ $1.45\times10^{3}\ \frac{J}{mol} = 145\ \frac{kJ}{mol} = E_a$
Check:	most activation energies are tens to hundreds of kJ/mol – so the answer is reasonable

Collision Theory of Kinetics

- for most reactions, in order for a reaction to take place, the reacting molecules must collide into each other.
- once molecules collide they may react together or they may not, depending on two factors -

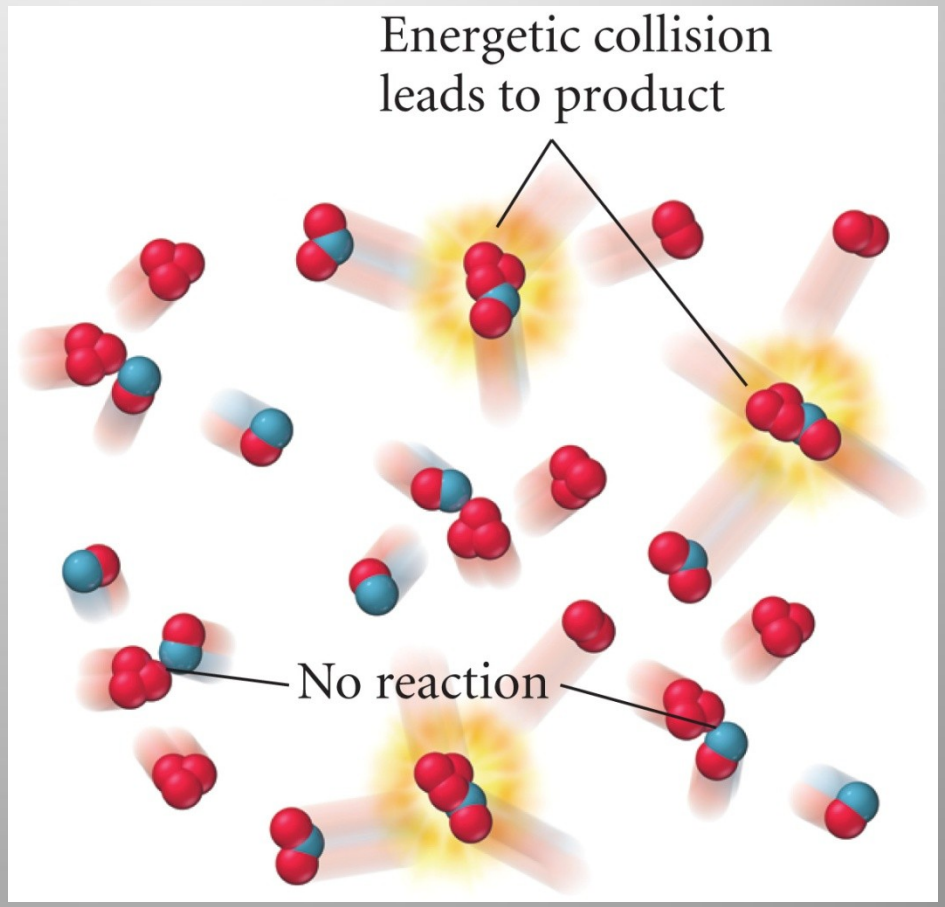
1. whether the collision has enough energy to "break the bonds holding reactant molecules together";
2. whether the reacting molecules collide in the proper orientation for new bonds to form.

Effective Collisions

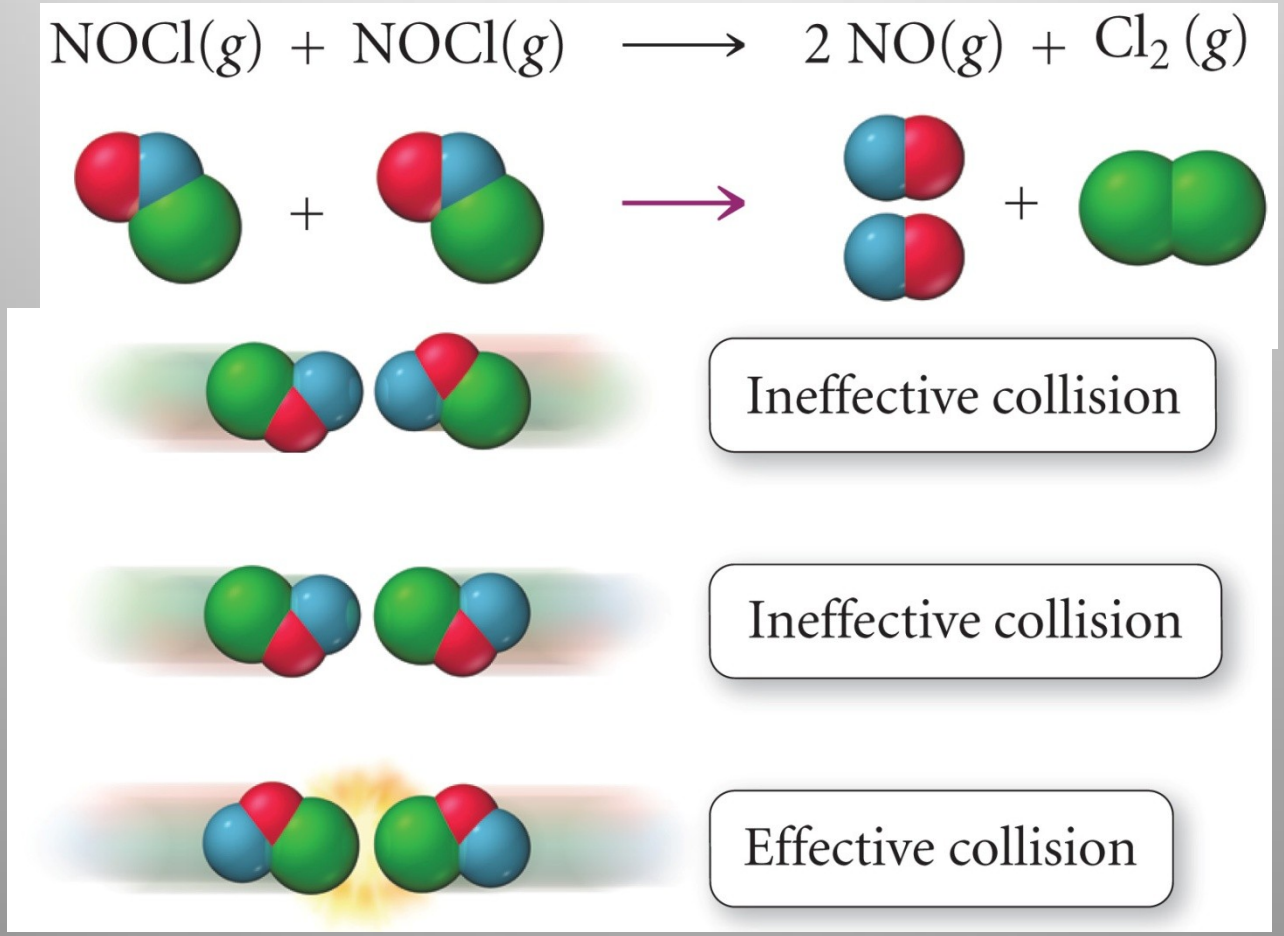
- collisions in which these two conditions are met (and therefore lead to reaction) are called **effective collisions**
- the higher the frequency of effective collisions, the faster the reaction rate
- when two molecules have an effective collision, a temporary, high energy (unstable) chemical species is formed - called an **activated complex** or **transition state**

Effective Collisions Kinetic Energy Factor

for a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that when they collide it can form the activated



Effective Collisions Orientation Effect



Collision Theory and the Arrhenius Equation

- *A* is the factor called the **frequency factor** and is the number of molecules that can approach overcoming the energy barrier
- there are two factors that make up the frequency factor – the **orientation factor (*p*)** and the **collision frequency factor (*z*)**

$$k = A\left(e^{\frac{-E_a}{RT}}\right) = pze^{\frac{-E_a}{RT}}$$

Orientation Factor

- the proper orientation results when the atoms are aligned in such a way that the old bonds can break and the new bonds can form
- the more complex the reactant molecules, the less frequently they will collide with the proper orientation
  - reactions between atoms generally have $p = 1$
  - reactions where symmetry results in multiple orientations leading to reaction have p slightly less than 1
- for most reactions, the orientation factor is less than 1
  - for many, $p << 1$
  - there are some reactions that have $p > 1$ in which an electron is transferred without direct collision

Radioactive Decay Rates

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

$$\text{Decay rate} = \frac{\Delta N}{\Delta t} = kN$$

N is the number of radioactive nuclei

k is the decay constant

Radioactive Decay Rates

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

$$\text{Decay rate} = \frac{\Delta N}{\Delta t} = kN$$

$$\ln\left(\frac{N_t}{N_0}\right) = -kt \qquad t_{1/2} = \frac{0.693}{k}$$

Reaction Mechanisms*****

Reaction Mechanism: A sequence of reaction steps that describes the pathway from reactants to products.

Elementary Reaction (step): A single step in a reaction mechanism.

An **elementary reaction** describes an individual molecular event. Each event cannot be broken down into simpler steps.

The **overall reaction** describes the reaction stoichiometry and is a summation of the elementary reactions.

Reaction Mechanisms

- we generally describe chemical reactions with an equation listing all the reactant molecules and product molecules
- but the probability of more than 3 molecules colliding at the same instant with the proper orientation and sufficient energy to overcome the energy barrier is negligible
- most reactions occur in a series of small reactions involving 1, 2, or at most 3 molecules
- describing the series of steps that occur to produce the overall observed reaction is called a **reaction mechanism**
- knowing the rate law of the reaction helps us understand the sequence of steps in the mechanism

A Reaction Mechanism Example

- Example Overall Reaction:

$$H_{2(g)} + 2\ ICl_{(g)} \rightarrow 2\ HCl_{(g)} + I_{2(g)}$$

- Two Step Mechanism:

1) $H_{2(g)} + ICl_{(g)} \rightarrow HCl_{(g)} + \cancel{HI_{(g)}}$
2) $\cancel{HI_{(g)}} + ICl_{(g)} \rightarrow HCl_{(g)} + I_{2(g)}$

- notice that the HI is a product in Step 1, but then a reactant in Step 2
- since HI is made but then consumed, HI does not show up in the overall reaction
- materials that are products in an early step, but then a reactant in a later step are called **intermediates**

Molecularity

- the number of reactant particles in an elementary step is called its **molecularity**
- a unimolecular step involves 1 reactant particle
- a bimolecular step involves 2 reactant particles
  - though they may be the same kind of particle
- a termolecular step involves 3 reactant particles
  - though these are exceedingly rare in elementary steps

Rate Laws for Elementary Steps

- each step in the mechanism is like its own little reaction – with its own activation energy and own rate law
- the rate law for an overall reaction must be determined experimentally
- but the rate law of an elementary step can be deduced from the equation of the step

$H_2(g) + 2\ ICl(g) \rightarrow 2\ HCl(g) + I_2(g)$

1) $H_2(g) + ICl(g) \rightarrow HCl(g) + HI(g)$ Rate = $k_1[H_2][ICl]$

2) $HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g)$ Rate = $k_2[HI][ICl]$

Rate Laws of Elementary Steps

TABLE 13.3 Rate Laws for Elementary Step

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \longrightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \longrightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event.**

unimolecular reaction: $O_3^*(g) \longrightarrow O_2(g) + O(g)$

$$\text{rate} = k[O_3]$$

bimolecular reaction: $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$

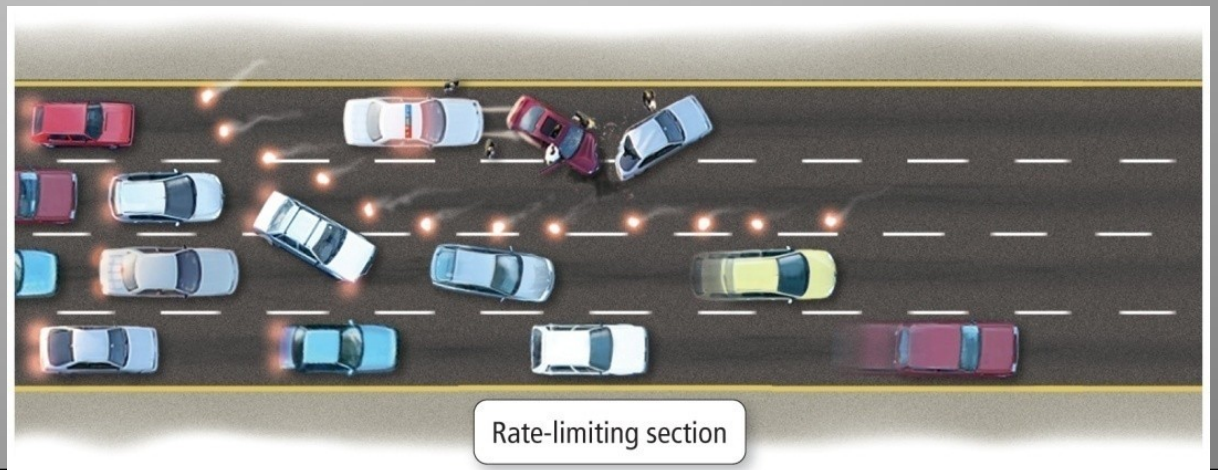
$$\text{rate} = k[O_3][O]$$

termolecular reaction: $O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$

$$\text{rate} = k[O]^2[M]$$

Rate Determining Step

- in most mechanisms, one step occurs slower than the other steps
- the result is that product production cannot occur any faster than the slowest step – the step determines the rate of the overall reaction
- we call the slowest step in the mechanism the **rate determining step**
  - the slowest step has the largest activation energy
- the rate law of the rate determining step determines the rate law of the overall reaction



Another Reaction Mechanism

Experimental evidence suggests that the reaction between NO_2 and CO takes place by a two-step mechanism:

$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ **elementary reaction**

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ **elementary reaction**

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ **overall reaction**

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ $\text{Rate}_{obs} = k[NO_2]^2$

1) **Slow** $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$ Rate = $k_1[NO_2]^2$

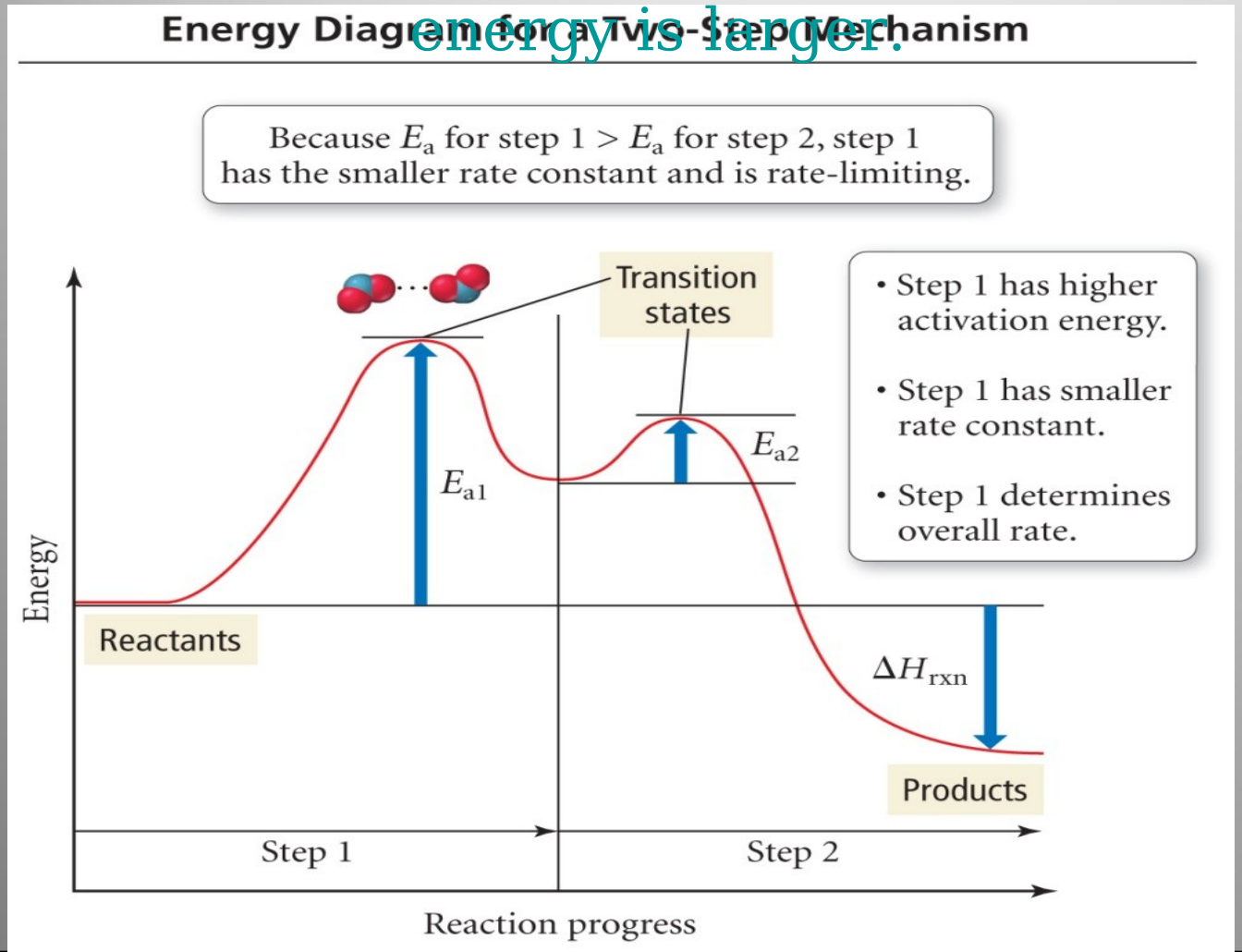
Fast

2) $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ Rate =

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

$$Rate_{obs} = k[NO_2]^2$$

The first step is slower than the second step because its activation energy is larger.


Energy Diagram for a Two-Step Mechanism
Because E_a for step 1 > E_a for step 2, step 1 has the smaller rate constant and is rate-limiting.
Transition states
• Step 1 has higher activation energy.
• Step 1 has smaller rate constant.
• Step 1 determines overall rate.
E_{a1}
E_{a2}
Energy
Reactants
ΔH_{rxn}
Products
Step 1
Step 2
Reaction progress

The first step in this mechanism is the rate determining step.

The rate law of the first step is the same as the rate law of the overall reaction.

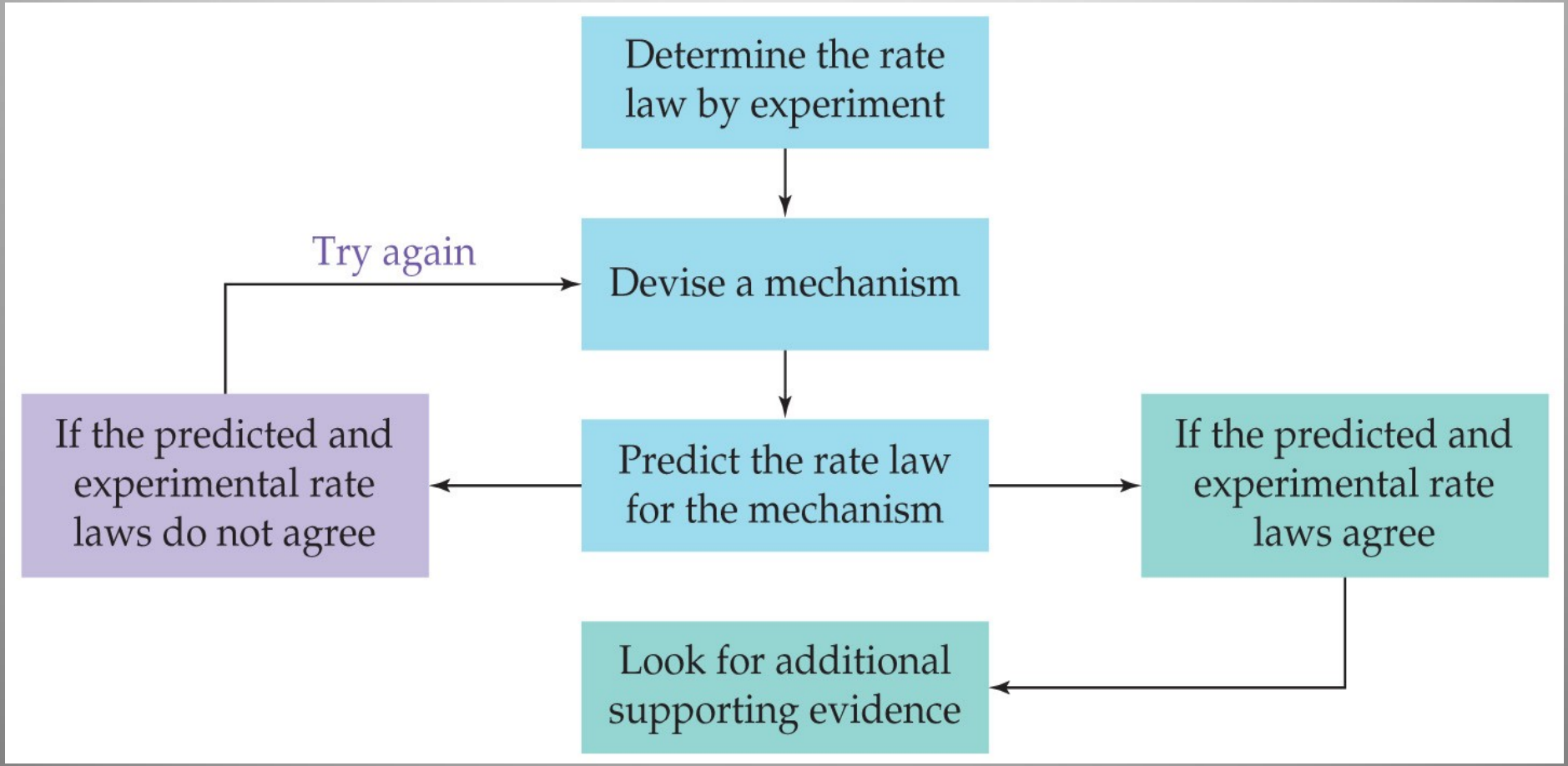
Validating a Mechanism

- in order to validate (not prove) a mechanism, two conditions must be met:

1. the elementary steps must sum to the overall reaction
2. the rate law predicted by the mechanism must be consistent with the experimentally observed rate law

Rate Laws for Overall Reactions

Procedure for Studying Reaction Mechanisms


Determine the rate law by experiment
Devise a mechanism
Try again
Predict the rate law for the mechanism
If the predicted and experimental rate laws do not agree
If the predicted and experimental rate laws agree
Look for additional supporting evidence

Mechanisms with a Fast Initial Step

- when a mechanism contains a fast initial step, the rate limiting step may contain intermediates
- when a previous step is rapid and reaches equilibrium, the forward and reverse reaction rates are equal – so the concentrations of reactants and products of the step are related
  - and the product is an intermediate
- substituting into the rate law of the RDS will produce a rate law in terms of just reactants

An Example

$$2\ NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} N_2O_{2(g)} \qquad \textbf{Fast}$$

$$H_{2(g)} + N_2O_{2(g)} \rightarrow H_2O_{(g)} + N_2O_{(g)} \qquad \textbf{Slow}$$

Rate = $k_2[H_2][N_2O_2]$

$$H_{2(g)} + N_2O_{(g)} \rightarrow H_2O_{(g)} + N_{2(g)} \qquad \textbf{Fast}$$

$H_{2(g)} + 2\ NO_{(g)} \rightarrow 2\ H_2O_{(g)} + N_{2(g)}$ $\quad Rate_{obs} = k[H_2][NO$

for Step 1 $Rate_{forward} = Rate_{reverse}$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

$$Rate = k_2[H_2][N_2O_2]$$

$$Rate = k_2[H_2]\frac{k_1}{k_{-1}}[NO]^2$$

$$Rate = \frac{k_2 k_1}{k_{-1}}[H_2][NO]^2$$

Show that the proposed mechanism for the reaction $2O_{3(g)} \rightarrow 3O_{2(g)}$ matches the observed rate law

Rate = $k[O_3]^2[O_2]^{-1}$

$$O_{3(g)} \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} O_{2(g)} + O_{(g)} \qquad \text{Fast}$$

$$O_{3(g)} + O_{(g)} \rightarrow 2\,O_{2(g)} \qquad \text{Slow} \qquad \text{Rate} = k_2[O_3][O]$$

for Step 1 $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

$$k_1[O_3] = k_{-1}[O_2][O]$$

$$[O] = \frac{k_1}{k_{-1}}[O_3][O_2]^{-1}$$

$$\text{Rate} = k_2[O_3]\frac{k_1}{k_{-1}}[O_3][O_2]^{-1}$$

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}}[O_3]^2[O_2]^{-1}$$

Catalysts

- catalysts are substances that affect the rate of a reaction without being consumed
- catalysts work by providing an alternative mechanism for the reaction
  - with a lower activation energy
- catalysts are consumed in an early mechanism step, then made in a later step

Mechanism without catalyst Mechanism with catalyst

$O_{3(g)} + O_{(g)} \rightarrow 2\ O_{2(g)}$ **VSlow**

$Cl_{(g)} + O_{3(g)} \Leftrightarrow O_{2(g)} + ClO_{(g)}$ **Fa**

$ClO_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl_{(g)}$ **Slo**

Catalysis

A catalyst is used in one step and regenerated in a later step. Since the catalyst is involved in the **rate-determining step**, it often appears in the rate law.

$$\text{rate} = k[H_2O_2][I^{1-}]$$

$H_2O_2(aq) + I^{1-}(aq) \longrightarrow H_2O(l) + IO^{1-}(aq)$ **rate-determining step**

$H_2O_2(aq) + IO^{1-}(aq) \longrightarrow H_2O(l) + O_2(g) + I^{1-}(aq)$ **fast step**

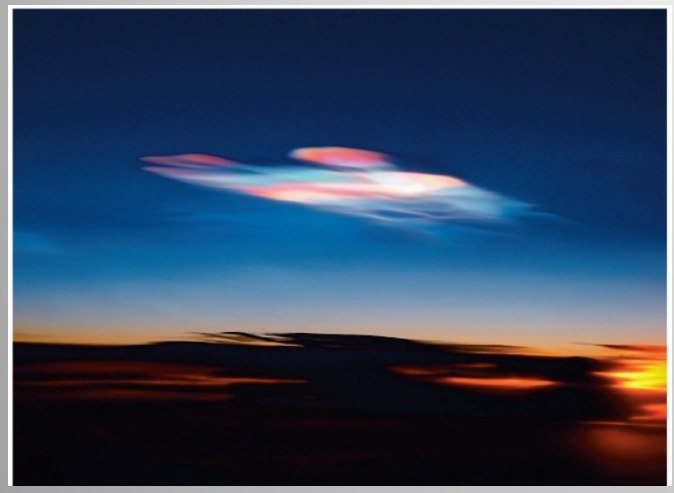
$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$ **overall reaction**

The rate of decomposition of aqueous hydrogen peroxide can be monitored qualitatively by collecting the evolved oxygen gas in a balloon.

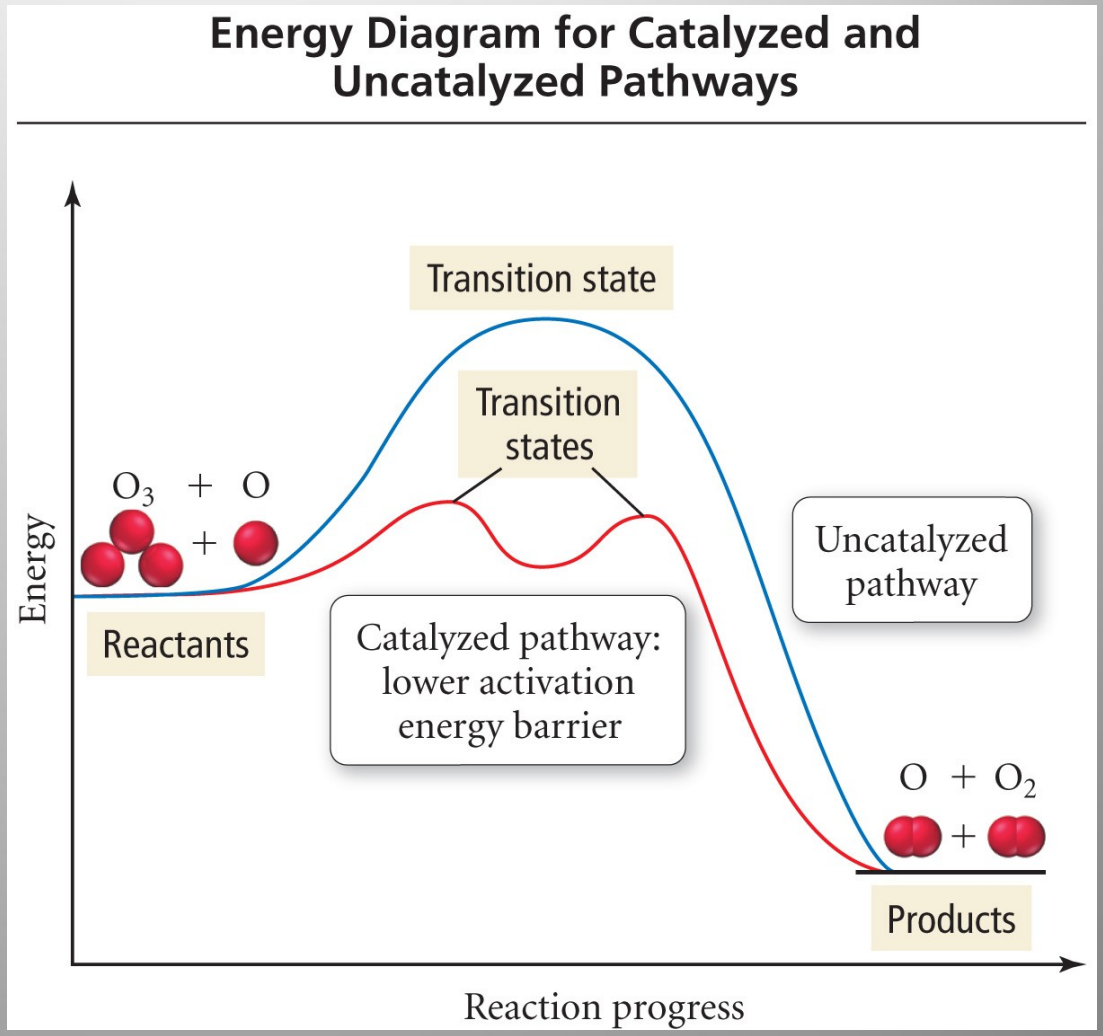
In the absence of a catalyst, little O_2 is produced.

After addition of aqueous sodium iodide, the balloon rapidly inflates with O_2.

Energy Profile of Catalyzed Reaction

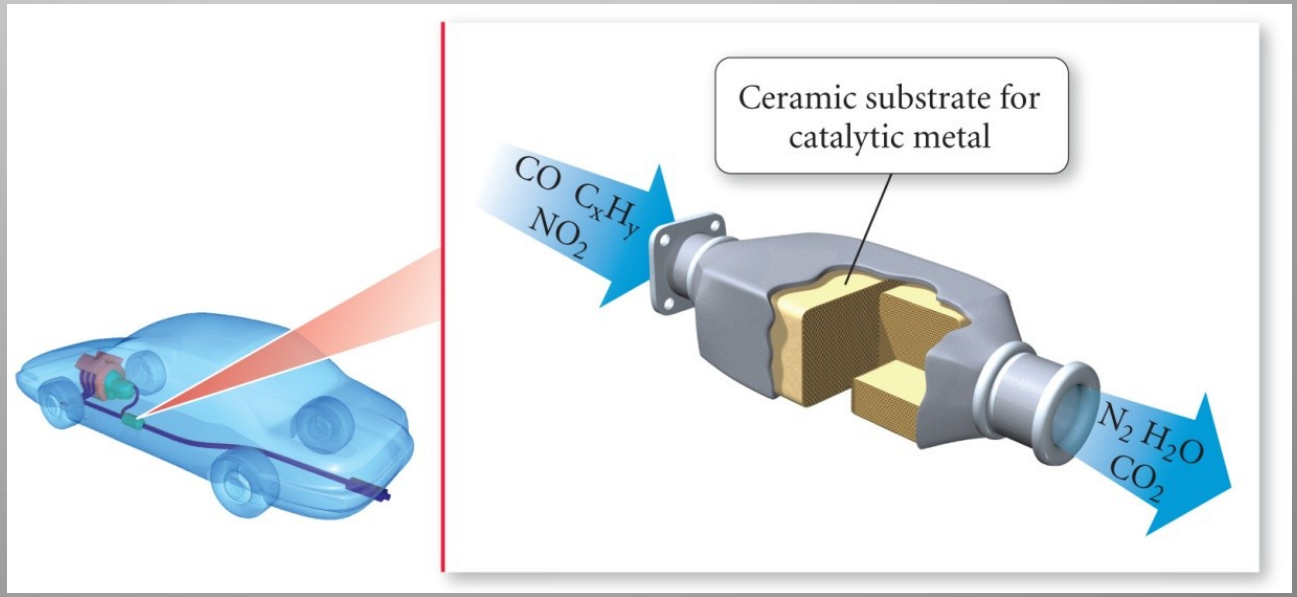


polar stratospheric clouds contain ice crystals that catalyze reactions that release Cl from atmospheric chemicals



Catalysts

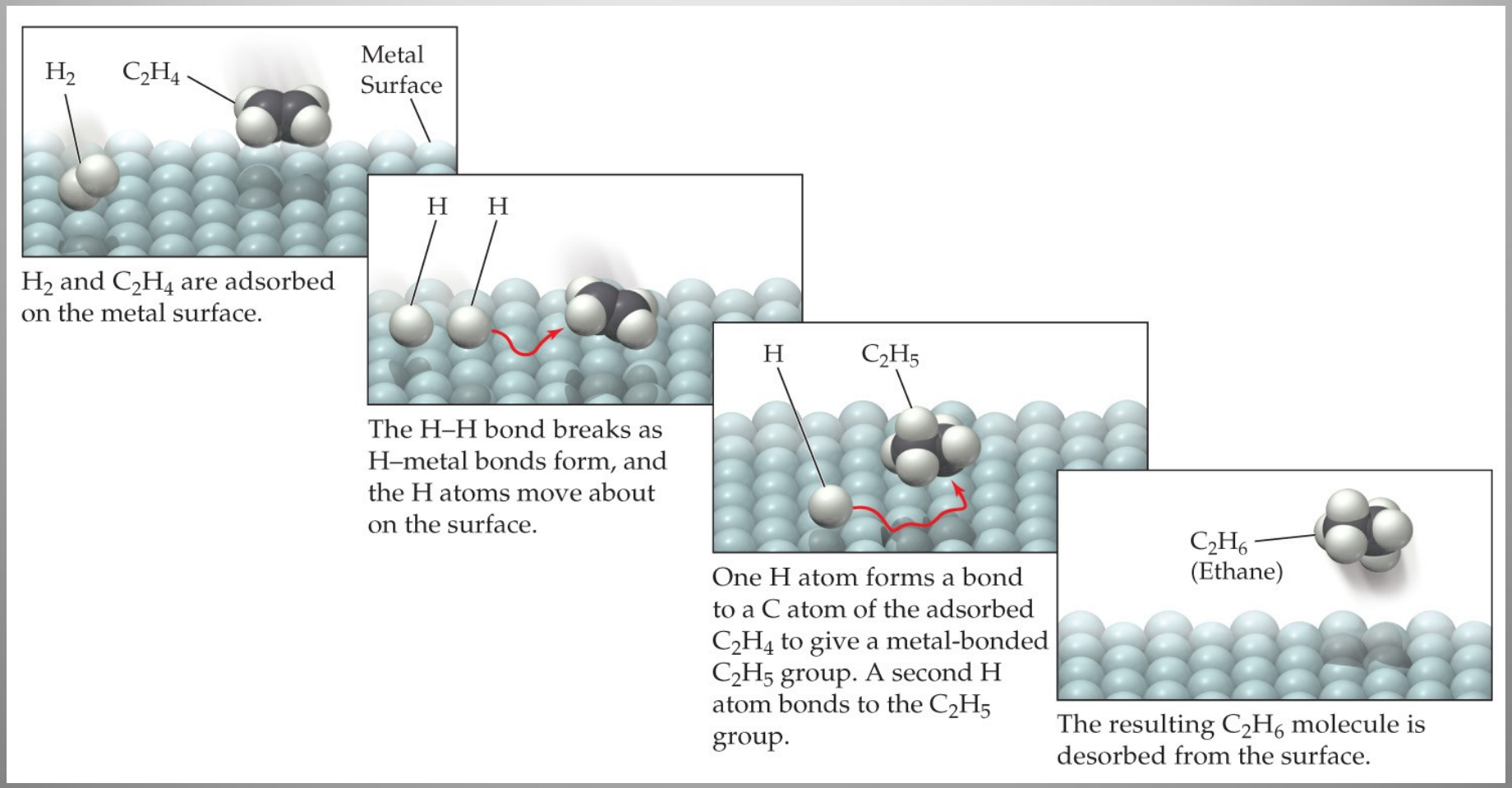
- **homogeneous catalysts** are in the same phase as the reactant particles
  - $Cl_{(g)}$ in the destruction of $O_{3(g)}$
- **heterogeneous catalysts** are in a different phase than the reactant particles
  - solid catalytic converter in a car's exhaust system



Heterogeneous Catalysts

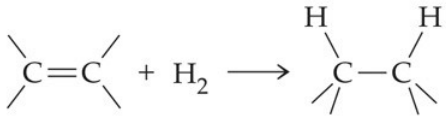
Catalytic Hydrogenation

$H_2C{=}CH_2 + H_2 \rightarrow CH_3CH_3$

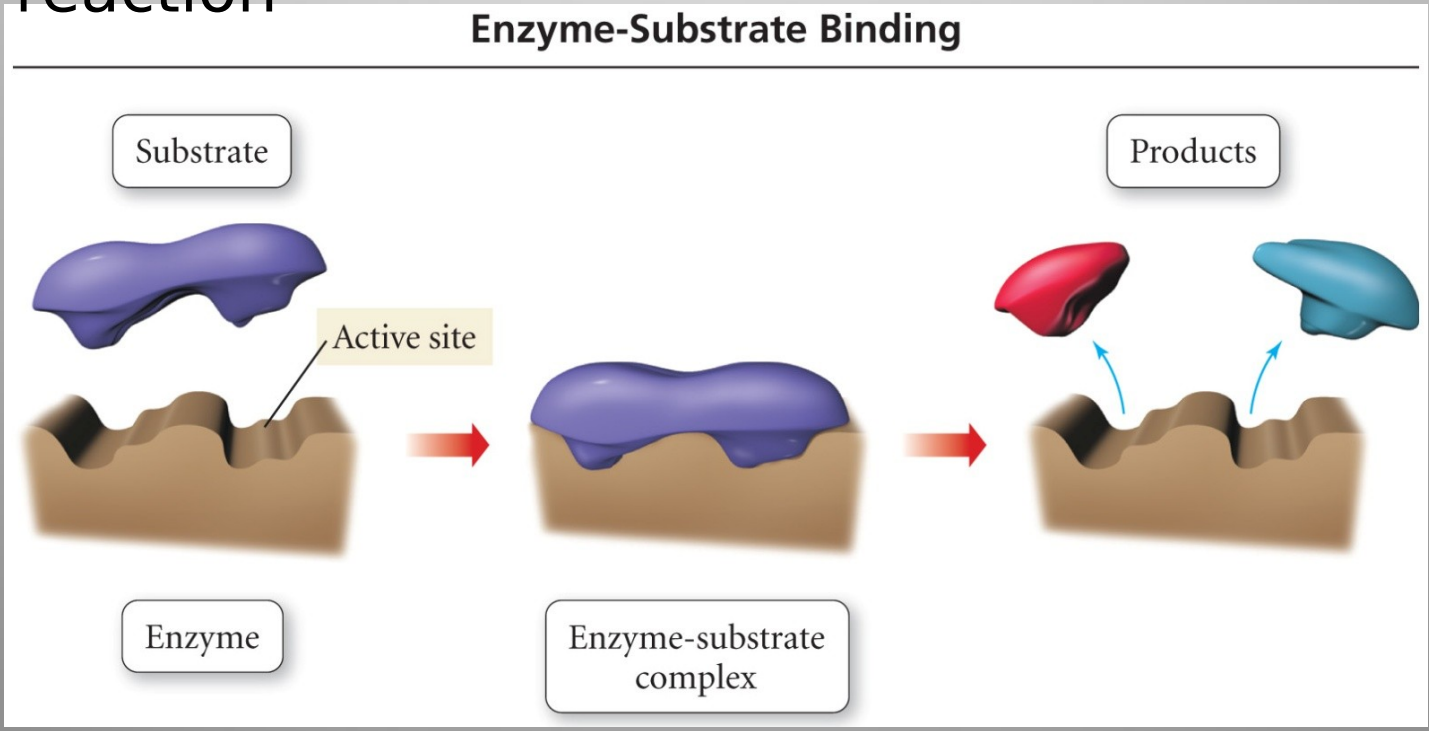

H2
C2H4
Metal Surface
H2 and C2H4 are adsorbed on the metal surface.
H
H
The H–H bond breaks as H–metal bonds form, and the H atoms move about on the surface.
H
C2H5
One H atom forms a bond to a C atom of the adsorbed C2H4 to give a metal-bonded C2H5 group. A second H atom bonds to the C2H5 group.
C2H6
(Ethane)
The resulting C2H6 molecule is desorbed from the surface.

Homogeneous and Heterogeneous Catalysts

TABLE 12.6 Some Heterogeneous Catalysts Used in Commercially Important Reactions

Reaction	Catalyst	Commercial Process	End Product: Commercial Uses
$2\,SO_2 + O_2 \rightarrow 2\,SO_3$	Pt or V_2O_5	Intermediate step in the contact process for synthesis of sulfuric acid	H_2SO_4: Manufacture of fertilizers, chemicals; oil refining
$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$	Pt and Rh	First step in the Ostwald process for synthesis of nitric acid	HNO_3: Manufacture of explosives, fertilizers, plastics, dyes, lacquers
$N_2 + 3\,H_2 \rightarrow 2\,NH_3$	Fe, K_2O, and Al_2O_3	Haber process for synthesis of ammonia	NH_3: Manufacture of fertilizers, nitric acid
$H_2O + CH_4 \rightarrow CO + 3\,H_2$	Ni	Steam–hydrocarbon re-forming process for synthesis of hydrogen	H_2: Manufacture of ammonia, methanol
$CO + H_2O \rightarrow CO_2 + H_2$	ZnO and CuO	Water-gas shift reaction to improve yield in the synthesis of H_2	H_2: Manufacture of ammonia, methanol
$CO + 2\,H_2 \rightarrow CH_3OH$	ZnO and Cr_2O_3	Industrial synthesis of methanol	CH_3OH: Manufacture of plastics, adhesives, gasoline additives; industrial solvent
	Ni, Pd, or Pt	Catalytic hydrogenation of compounds with C=C bonds, as in conversion of unsaturated vegetable oils to solid fats	Food products: margarine, shortening

- because many of the molecules are large and complex, most biological reactions require a catalyst to proceed at a reasonable rate
- protein molecules that catalyze biological reactions are called **enzymes**
- enzymes work by adsorbing the substrate reactant onto an active site that orients it for reaction



Enzymatic Hydrolysis of Sucrose